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Treatment of Electroplating Wastes by Reverse Osmosis

American Electroplaters' Society, East Orange, N J

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September 1976

TREATMENT OF ELECTROPLATING WASTES BY REVERSE OSMOSIS

Submitted by

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is a product of the above efforts. These studies were undertaken to evaluate the feasibility of commercially available reverse osmosis membranes for achieving closed-loop pollution abatement of metal finishing rinse wastewaters. Reverse osmosis pilot plant testing was carried out to recover the chemicals while purifying the water for reuse on nine major metal finishing rinse waters. The Metals and Inorganic Chemicals Branch, Industrial Pollution Control Division may be contacted for further information on this subject.

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ABSTRACT

Reverse osmosis treatment of plating bath rinse waters has been examined. Emphasis has been placed on closed-loop operation with recycle of purified water for rinsing, and return of plating chemical concentrate to the bath. Three commercially available membrane configurations have been evaluated experimentally; tubular (cellulose acetate membrane), spiral-wound (cellulose acetate membrane), and hollow-fiber (polyamide membrane). Tests were conducted with nine different rinse wastes prepared by dilution of actual plating baths. Advantages and limitations of the reverse osmosis process and specific membranes and configurations are discussed. Promising, as well as unattractive, applications are indicated.

This report was submitted in partial fulfillment of EPA Project Number R800945 (formerly 12010 HQJ) by the American Electroplaters' Society, Inc. under the partial sponsorship of the Environmental Protection Agency.

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SECTION I
CONCLUSIONS

1. Reverse osmosis (RO) appears to be an attractive process for closed-loop treatment of plating rinse wastes. Baths for which technical feasibility has been demonstrated are given in Table 1, together with any limitations. In addition, systems which cannot be treated by RO at present are also indicated.

2. At present, the spiral-wound and hollow-fiber membrane module configurations are preferred for plating applications because they are more compact and less expensive than tubular modules. Membrane selection is based primarily on the pH of the rinse-water concentrate: the cellulose acetate membrane can be used from pH 2.5-7; the polyamide membrane can be used from pH 4-11. In the region of pH overlap, neither membrane has an overriding advantage over the other.

3. The degree to which the recycled plating chemicals would be concentrated by RO in a commercial-scale installation must be determined on a case-by-case basis. Important factors include: the ratio of water loss from plating bath evaporation to dragout; the maximum concentration limit physically obtainable by RO; and the relative economic attractiveness of RO concentration at high solids (low flux) vs. auxiliary evaporation.

4. The degree to which rinse waters would be purfied in a commercial installation would also be determined on a case-by-case basis and depend on the water purity required for effective rinsing. Considerations for achieving the required rinsing include adding a final rinse stage outside the closed-loop system, staging the permeate stream in RO units, and/or adding a final purification step, e.g., ion exchange, to treat the permeate before reuse.

Table 1. Evaluation of RO for Systems Tested

Attractive Systems (For Treatment)	Limitations
Watts-Type Nickel	Boric acid selectively permeates membranes.
Nickel Sulfamate	Boric acid selectively permeates membranes.
Copper Pyrophosphate	Possible decomposition of pyrophosphate.
Nickel Fluoborate	Boric acid selectively permeates membranes.
Zinc Chloride	Need evaporation to close loop.
Copper Cyanide	Need low-pH bath for current membranes.
Zinc Cyanide	Need low-pH bath for current membranes; need evaporation to close loop.
Cadmium Cyanide	Need low-pH bath for current membranes; need evaporation to close loop.
Unattractive Systems (Not For Treatment)	**Limitations**
Chromic Acid	Attacks and destroys all membranes unless neutralized.
Very-high pH Cyanide Baths	Attack and destroy all membranes commercially available. Newer membranes under development show promise for treating high-pH cyanide baths.

5. The effect of impurity buildup in RO closed-loop operations varies for each bath, and will require pilot-scale studies for determination. It is believed, however, that purification techniques used for evaporative closed-loop systems will be equally suitable for RO systems, since the purification problems are the same.

6. The effect of the selective permeation of certain plating bath components in some systems will require proportionally larger additions to the bath of those chemicals selectively permeated.

SECTION II
RECOMMENDATIONS

While the results of this research indicate that reverse osmosis (RO) appears promising for the treatment of electroplating rinse waters, it is necessary to demonstrate the capabilities of RO under realistic conditions before recommending its use in the plating industry. Therefore, it is recommended that field demonstrations be conducted with the plating baths that appear to be attractive candidates for treatment by RO. The field demonstration should evaluate:

1. membrane life under practical operating conditions
2. effect of closed-loop treatment on the level of bath impurities, and their effect on plating characteristics
3. means of controlling bath impurities
4. economics of closed-loop treatment by RO.

Other membranes should be tested as they become available. Of particular interest are membranes that can tolerate very high or low pH's and withstand oxidizing conditions.

SECTION III
BACKGROUND

GENERAL

Industrial pollution of our streams and waterways has become an increasingly acute problem. Electroplating and metal finishing waste streams are significant contributors to this problem, either directly, due to their content of toxic or corrosive chemicals; or indirectly, due to the deleterious effect of these chemicals on biological waste treatment systems. The Federal Water Quality Control Act Amendments of 1972 call for the application of "best practicable" technology by 1977 and "best available" technology by 1983 to alleviate the problem. In addition, the act declares that it is the national goal to eliminate the discharge of pollutants into the navagable waters of the United States by 1985.

There is ample technology available for treating metal finishing wastes to any required degree of detoxification. The problem of reducing contaminants to a specified level is, therefore, one of economic feasibility rather than technological feasibility. One single process will obviously not solve all pollution problems for all platers. A variety of waste treatment facilities will be installed in the future with the exact facility for any plater depending on a balance of economic factors for his particular plating operation.

The treatment of plating wastes can be broadly classified according to whether plating chemicals are destroyed or recovered. Destructive processes include chemical or electrolytic treatment and are aimed primarily at reducing contaminant levels in effluent streams rather than reclaiming chemicals that are lost in bath dragout and subsequent rinsing operations. On the other hand,

recovery processes treat effluent streams in such a way that ionic species are recovered in a form suitable either for recycle to the plating operation or for other reuse. Examples of recovery processes are ion exchange (if the exchange resins are regenerated to yield recyclable materials), evaporation, RO, and, more recently, electrodialysis. In many cases, waste streams that would ordinarily be discharged can be treated to reclaim useful metals.

Recovery processes offer considerable potential for an economically viable solution to the plating waste problem. As plating chemicals and disposal of solid wastes from destructive systems become increasingly more expensive, chemical recovery will be preferred to chemical destruction. Ideally, complete closed-loop operation is feasible with the recycle of purified water to rinsing operations and concentrated chemicals to plating baths.

Figure 1 shows a typical block diagram for closed-loop treatment of electroplating rinse water by RO. Any other recovery technique, e.g., evaporation, would be applied in a similar manner. Rinse water from the first rinse tank, which would otherwise be discharged to drain, is first treated to remove impurities, primarily particulates, and then pumped to the RO membrane concentrator. The concentrator separates the feed stream into a "concentrate" stream, containing a relatively high concentration of plating chemicals, and a "permeate" stream, containing purified water. Before returning the concentrate stream to the plating bath, it may be necessary to remove additional water by evaporation. The permeate stream is recycled to the final rinsing stage where makeup water is added to compensate for bath evaporation. It is necessary to use deionized makeup water in order to avoid a buildup in the bath of impurities contained in untreated water. The operation of a closed-loop process such as shown in Figure 1 not only eleminates the problem of rinse water disposal but also recovers valuable plating chemicals and reduces the amount of purchased water required for rinsing.

Over the past several years RO has received increased attention as an attractive recovery process for electroplating waste streams [1-4]. Application has been largely limited to the treatment of Watts-type nickel rinses, although more recently, the treatment of total plating shop effluents and a few

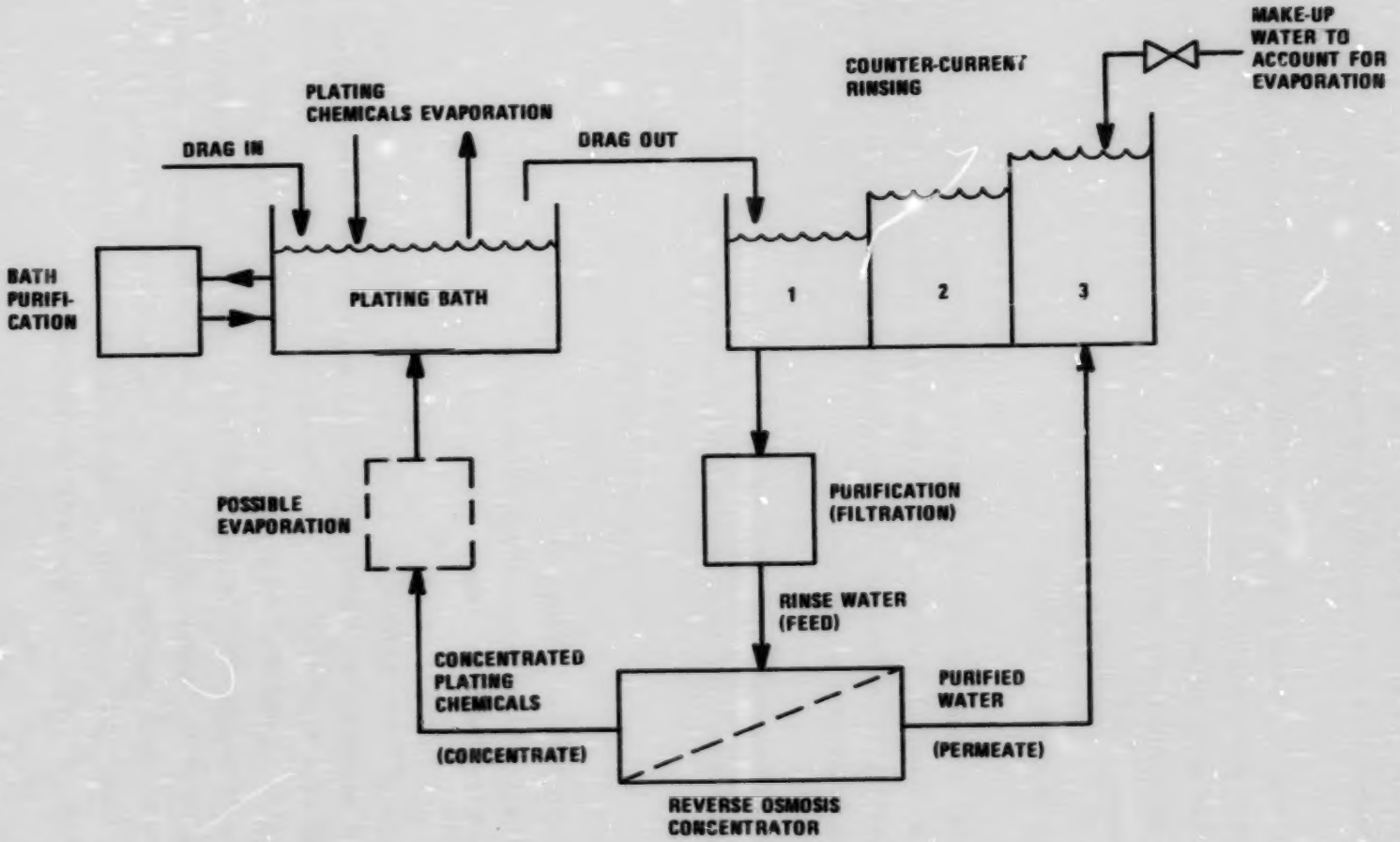

Figure 1. Generalized Process Flow Schematic

other selected rinse waters have been considered. However, published data on the RO treatment of plating wastes are limited.

This report presents data for the RO treatment of a number of actual plating bath rinse wastes using three different commercially available RO modules. These data can be used to determine the current performance characteristics and to estimate the economic feasibility of RO for treatment of a specific plating waste.

PRINCIPLES OF REVERSE OSMOSIS

A brief summary of reverse osmosis theory follows. A more detailed treatment can be found in Reference 5. Membrane performance is evaluated in terms of the quantity (flux) and the quality (rejection) of the permeate obtained under conditions of the experiment.

Flux, (J) is the volume flow of permeate (water) per unit membrane area and is proportional to the effective pressure driving force:

$$J = K (\Delta P - \Delta \Pi) \qquad (1)$$

where K = the membrane constant;
ΔP = difference in applied pressure across the membrane
$\Delta \Pi$ = difference in osmotic pressure across the membrane.

Flux is an important factor since the size of the membrane system, for a given plant capacity, is inversely proportional to flux. From equation (1) it can be seen that flux decreases with increasing feed concentration; since II is approximately proportional to feed concentration. At a given feed solids level, flux is higher for plating chemicals which form high molecular weight complexes, since II depends on molarity. Since it is generally desirable to concentrate a rinse water to as high a solids level as possible, it is important that the effective pressure driving force be as large as possible. This favors the use of high pressure membrane equipment.

The percent rejection, R, is defined as:

$$R = \frac{C_{feed} - C_{permeate}}{C_{feed}} \times 100.$$

Rejection depends primarily on membrane type. In practice, for plating applications, one selects the highest rejection membrane available in order to maximize the recovery of chemicals and to maximize the product water purity.

Rejection decreases with increasing feed concentration, since the solute flux is, to a first approximation, a function only of solute concentration. However, water flux decreases with increasing solute concentration (see Reference 5 for details).

APPLICATION OF REVERSE OSMOSIS TO PLATING WASTE TREATMENT

Previous studies have shown that RO treatment is both technically and economically feasible for some plating waste streams. [1-4] Particular advantages of RO over other recovery processes are:

1. Low capital cost. The modular nature of RO units makes them particularly well-suited for small-scale installations.
2. Low energy cost. Only power for pumping is required.
3. Low labor cost. The process is simple to operate since it involves primarily the pumping of liquids.
4. Low space requirements. RO equipment is compact and operates continuously, requiring minimal tankage.

There are, however, some important limitations of RO specifically, and closed-loop recovery processes in general:

1. There is a limited pH range (about 2.5 - 12) over which current membranes can operate for extended periods. Treatment of streams outside this range requires neutralization, and the concentrate cannot, therefore, be directly recycled to the plating bath. As new membranes become available, the treatable pH range will undoubtedly

broaden. However, at present, the economics are not particularly attractive for the RO treatment of highly acidic or highly alkaline waste streams.

2. RO is incapable of concentrating solutions to very high concentrations. Concentration can be achieved by reverse osmosis only so long as the operating pressure exceeds the osmotic pressure of the solution. Thus, the degree of concentration provided by a particular module is limited by its maximum operating pressure (Table 2).

   The severity of this limitation depends on the specific osmotic pressure of the bath and the ratio of bath evaporation to dragout. For plating baths with substantial evaporation (e.g., Watts nickel, nickel sulfamate, and copper cyanide) a high degree of concentration is not required and RO is capable of providing a concentrate stream which can be recycled to the bath directly. For ambient-temperature plating baths, it may be necessary to use evaporation in conjunction with RO in order to achieve sufficient concentration for direct recycle.

3. No membrane is completely effective in rejecting ionic solutes. Specific solutes may permeate the membrane at rates sufficient to give unacceptably high solute concentrations in the permeate for final rinsing (or discharge). Additional treatment of the permeate, for example by an additional RO stage or ion exchange, may be required. The seriousness of this limitation must, of course, be evaluated on a case-by-case basis.

4. As in any closed-loop recovery process, a buildup in bath impurities must be anticipated. Impurities that were formerly removed by bath dragout and rinsing are, in closed-loop operation, recovered along with plating chemicals and recycled to the bath. This could result in a long-term buildup of impurities in the system which might have an adverse effect on plating quality. As in Figure 1, it may be necessary to use various purification systems, such as filtration, adsorption, chemical treatment, electrolysis, and aeration, to keep impurities at acceptably low levels. These systems are further discussed under "Purification Techniques" (page 16). It is anticipated that the same purification schemes used for evaporative closed-loop

Table 2. Commercially Available Membrane Systems

Type	Allowable pH range	Maximum operating pressure kg/cm^2	Approximate cost,[a] $/liter/day	Susceptibility to plugging by suspended solids	Space requirement
Hollow Fiber[b] (Polyamide Membrane)	4 to 12	29 (400 psig)	$0.084 ($ 0.32/gal/day)	very high	very low
Spiral Wound (Cellulose Acetate Membrane)	2.5 to 7	58 (800 psig)	$0.084 ($ 0.32/gal/day)	high	very low
Tubular (Generally Cellulose Acetate Membrane	2.5 to 7	109 (1500 psig)	$ 0.26 - 0.53 ($ 1 to 2/gal/day)	low	moderate

[a] Cost of membrane element alone, without pump, controls, piping, instrumentation, etc.

[b] A high-pressure, hollow-fiber module (duPont B-10) has recently become commercially available. It is capable of operating at 58 kg/cm^2 (800 psi) and uses the same membrane (polyamide) as the lower pressure module (duPont B-9).

operations will be suitable and adequate for use with RO closed-up systems.

MEMBRANE PROCESS EQUIPMENT

There are essentially three types of commercially available RO membrane configurations, all of which were examined in this study. The simplest type is the tubular module, which consists of a porous tubular support with the membrane cast in place or inserted into the support tube. The feed solution is pumped through the tube; the concentrate is removed downstream; and the permeate passes through the membrane/porous support composite into the surrounding collection shell. Figure 2 shows a tubular membrane module which consists of a bundle of tubes in one collection shell.

The spiral wound module contains a large membrane sheet(s) which, in order to obtain a compact design, is wound around a central permeate-collector tube. The feed solution is passed over one side of the sheet, and the permeate passes through the membrane, flows through the backing material and into the permeate-collector tube. The membrane cartridge construction is shown in Figure 3.

The hollow-fiber module consists of thousands of fine hollow fiber membranes (40-80μ dia) which are arranged in a bundle around a central porous tube as shown in Figure 4. The feed solution is introduced through this tube, passes over the outside of the fibers and is removed as concentrate. Water permeates through the fiber walls, flows through the hollow fibers, and is collected at one end of the unit.

Each of these modules has particular advantages and disadvantages as summarized in Table 2. The hollow-fiber and spiral-wound systems show cost advantages (in units of dollars per liter permeate per day) over the tubular system; however, they are more susceptible to plugging and fouling by suspended solids, requiring careful filtration of the feed. The tubular system has the advantage of a higher operating pressure which makes it a preferred system for feeds having a high osmotic pressure.

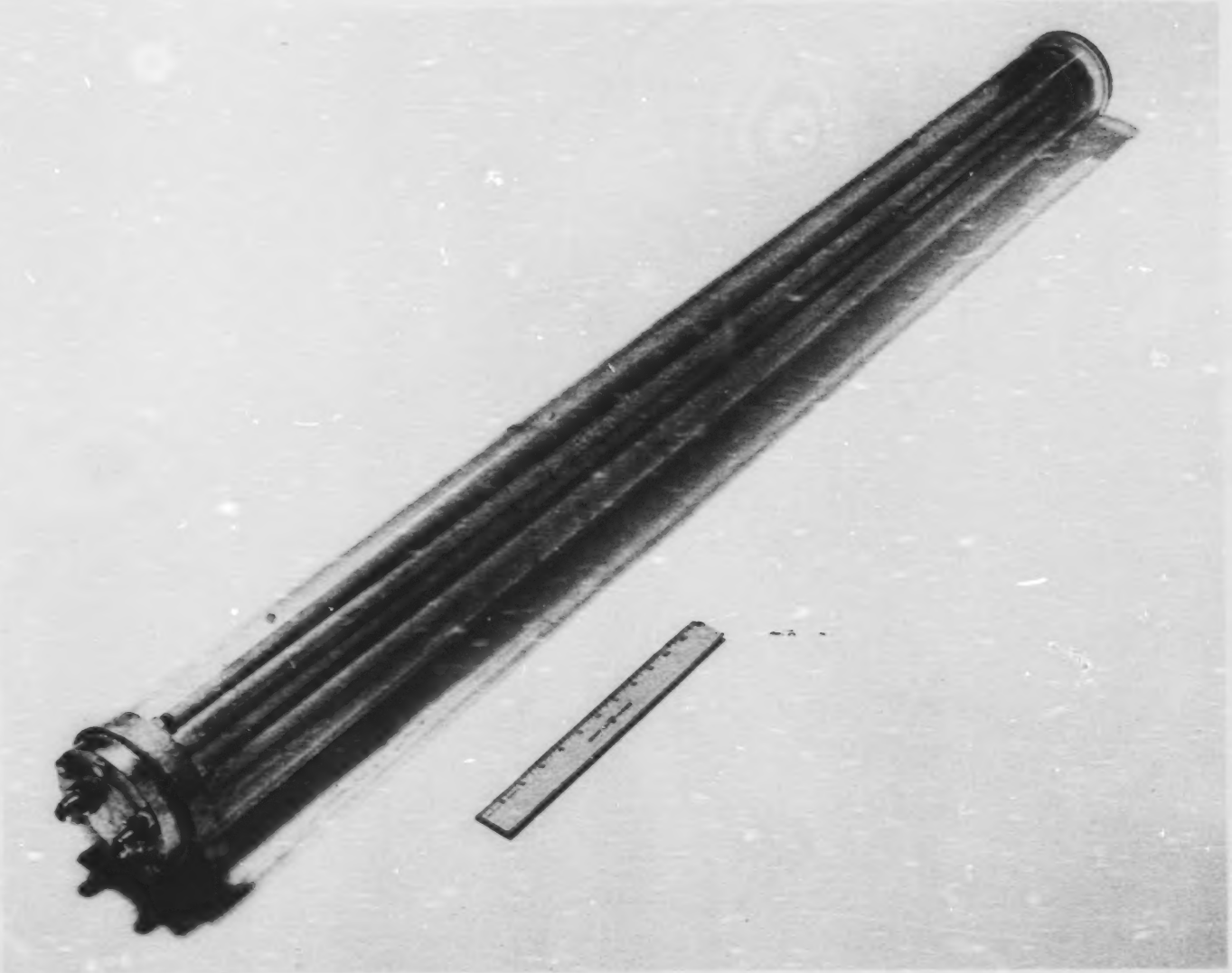

Figure 2. Tubular Membrane Module

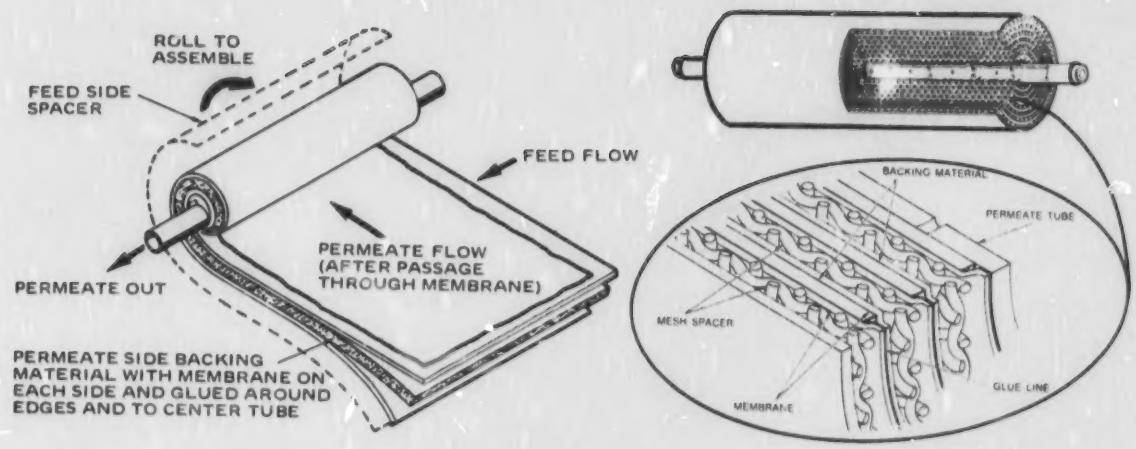

Figure 3. Spiral Wound Membrane Cartridge

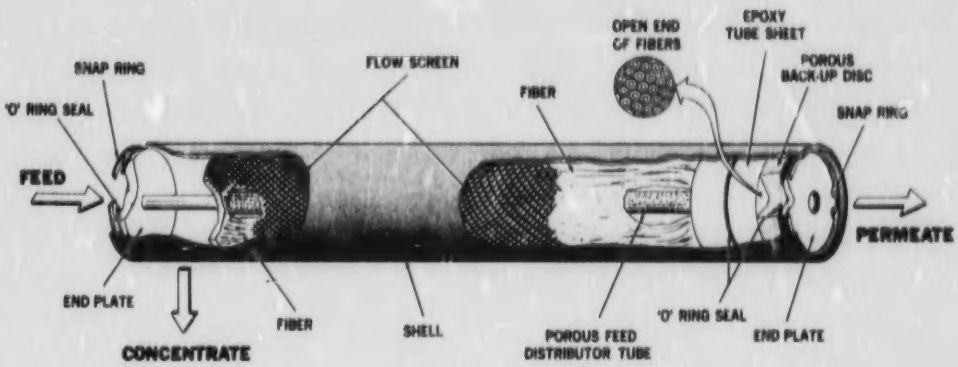

Figure 4. Permasep Hollow-fiber Permeator

There are a number of membrane materials presently under development, but only two are in commercial use. Of these two, (cellulose acetate and polyamide), cellulose acetate is the more widely applied. This membrane was originally developed for water desalination but has since been adopted for many industrial waste treatment applications. It exhibits excellent water permeation rates and high rejection of ionic species, but unfortunately it is limited to a fairly narrow pH range (2.5 - 7). Operation beyond this range hydrolizes the membrane and changes its structure, thereby destroying its ability to selectively pass water.

The other membrane material, duPont's polyamide, has been observed to show long operating life (three years) when operated over a pH range of 4 to 11. Thus this membrane, commercially available in the hollow-fiber configuration, appears to be especially attractive for the treatment of high pH wastes, such as cyanides, while the cellulose acetate membrane, commercially available in both the tubular and spiral-wound configurations, would be preferable for treatment of low pH wastes.

Since these kinds of considerations must be evaluated on a case-by-case basis, all three membrane systems were tested for all the plating baths studied (except where pH limitations were obvious and insurmountable).

PURIFICATION TECHNIQUES[6-10]

General

Regardless of what concentration process a closed-loop recovery system is based on (reverse osmosis, evaporation, ion exchange, or electrodialysis), a build-up in bath impurities can be expected. Impurities formerly kept at a low level by dragout from the bath are, in closed-loop operation, recovered and recycled to the bath along with the plating chemicals.

Purification is presently required for long-term baths and bright-dip baths, and current purification techniques should be adequate, if not ideal, because RO adds no new impurities to the system. Generalizations on purification are virtually impossible because each bath, each process, and

each ship, have different impurity problems. The impurities can, however, be divided into three general catagories: Suspended solids, organic contaminants, and inorganic contaminants.

Suspended solids are a problem in all baths because they result in roughness and pitting. Sources of suspended solids include anodes, chemical additions, improperly cleaned work, and airborne dust. Suspended solids are routinely removed from plating baths by various methods of filtration.

Organic contaminants in the bath affect the appearance of the deposit, especially in bright plating, and lower the efficiency of the bath. Sources include, organic decomposition products of brighteners and improperly cleaned work. The most common technique for removing organic contaminants is adsorption on activated carbon.

Inorganic contaminants show vastly different effects in different types of baths. Cyanide baths have a built-in protective mechanism because many metals complex with free cyanide (two exceptions are hexavalent chromium and lead). Acid baths have no such complexing agents, and any contaminant near or below the deposition potential of the plating material will co-deposit. Table 3 shows some of the problem inorganics for several baths. Inorganic contaminants can be removed by chemical or electrolytic purification.

Removal of Suspended Solids by Filtration

One type of filtration involves the use of depth-type cartridge filters to remove suspended solids. These filters retain particles as small as 1-30μ and consist of twisted yarn which is wound around a core to form diamond-shaped openings. Subsequent windings of yarn hold the fibers in place, and the openings get larger as winding continues because the same number of diamond shaped openings are included in each layer as the diameter increases. Because of this geometry, larger particles are retained on the exterior of the filter and smaller particles on the interior, thereby yielding a high surface area filter in a small volume. The filter-cartridge lifetime is, of course, dependent on the application. In general, filter systems are designed to have two 378 liters/hour (100 gallons/hour) cartridges for each 378 liters (100 gallons) of

Table 3. Some Impurities and Their Effect

Bath	Impurity	Effect
Chromium	Copper, Iron	Co-Precipitation
	Nickel, Zinc, Cadmium	Insenitive
	Trivalent Chromium	Increases bath resistance and may cause gray deposits
	Chlorides	Catalytic effect
Copper Sulfate	Arsenic, Antimony	Brittle and rough deposits
	Nickel, Iron	Reduces bath conductivity and may cause rough deposits
	Silicates (soluble)	May precipitate on work
Nickel Baths	Hexavalent Chrome, Copper, Zinc	Co-precipitate
Zinc Cyanide	Cadmium, Lead	Dull plate
	Copper	Dull plate and darkening of bright plate when nitric acid dipped

tank capacity. Typical lifetimes of 4-6 weeks can be expected for plating applications. The primary advantage of cartridge filters is their convenience of use.

Another type of filtration uses precoat filters and will retain particles as fine as 0.5-5μ. The filter consists of a porous support which is treated with a filter aid such as diatomaceous earth or some fibrous-type filter aid. Porous supports include; paper, cloth, ceramic, stone, sintered metal, wire mesh, and wound cartridges. The filter aid is precoated onto the porous support by forming a slurry of the filter aid with water or plating solution and filtering the slurry. During operation, the filter is back-washed manually when the pressure drop becomes excessive.

Granular depth filters (sand filters) can also be used for suspended solids removal. Sand filters are typically 61-76 cm. (24-30 in.) in depth with sands ranging from 0.45 to 1mm. in diameter. Both gravity-flow and pressurized vessels are available. Suspended solids are trapped in the interstices of the filter medium, and in some cases, formation of a surface cake at the top of the filter can aid in the removal of solids. As the filter bed becomes loaded with particulates, the burden or removal gradually shifts from the upper layers of the bed to the lower. Eventually, solids removal or pressure drop becomes unacceptable and the filter must be cleaned by backwashing. The advantages of the granular depth filter are its simplicity of design, operation, and maintenance. The disadvantage is that the quality of the filtrate generally decreases with time.

Adsorption

The most common adsorbent used in bath purification is activated carbon. It is commonly used to remove oil, grease, additive agents, and decomposition products of brighteners. Different types of carbon remove different organics, and suppliers of proprietary plating bath solutions will frequently supply specially mixed carbons for adsorbing the specific impurities found in such baths.

Activated carbon can be applied to the plating bath in several different ways:

1. Throw-away cartridges and canisters are commercially available.
2. Carbon can be used as the granular filter medium in a granular depth filter.
3. Carbon can be used as the filter aid in a precoat filter.
4. Batch treatment of a portion of the bath can be carried out in a separate mixing tank.
5. A carbon column can be used following a separate filtration system.

The final option is the most versatile since the filtration and adsorption systems can be designed, controlled, and maintained separately.

Another adsorbent is activated clay which is used to remove NH_4^+ from cobalt-nickel baths. Specific adsorbents are also available to remove certain inorganics.

Chemical Treatment

Two types of chemical treatment are oxidation and precipitation. Oxidation in this case, is performed using potassium permanganate or hydrogen peroxide. Potassium permanganate ($KMnO_4$) oxidizes many organics, including brightener decomposition products, and is reduced to MnO_2 in the process. MnO_2 has adsorptive properties, so this treatment preceding carbon adsorption is often effective. It is not universally effective, however, and sometimes is detrimental. Chemical treatment with $KMnO_4$ is performed with the solution at a pH of 1.5-2.5. The carbon is added while raising the pH of the solution to 4.5-5.0, and the solution is then filtered.

Hydrogen peroxide (H_2O_2) is a weaker oxidant than potassium permanganate, but has favorable decomposition products. The treatment is performed by adding 0.1-3.0 ml of 30% H_2O_2 to each liter of solution, agitating at 60°C (140°F) for 3 hours, adding carbon, and filtering.

Precipitation is used as a last resort in removing inorganics, and methods vary from bath to bath. In zinc cyanide plating, lead and cadmium can be

precipitated by maintaining a small excess of sodium polysulfide in the bath and copper can be removed by adding zinc dust and filtering after 2-3 hours.

Electrolytic Purification at Low Current-Density

This treatment is based on the phenomenon that many impurities cause specific effects at certain low current-density sites during plating. In fact, preferential co-deposition occurs at these low current-densities, so that a "dummy" cathode operated at low current will have deposited relatively more impurity than the plating material. Corrugated and flat plates are used for purification, and should be plated with the plating material first. The voltage used must not be too low, or no deposition takes place. Also, counter-potentials could be set up since only certain areas of the plate deposit impurities. The current must remain on at all times to prevent dissolution of impurities.

Treatment begins at 0.0028-0.0043 amps/cm^2 (0.02-0.03 amps/in^2) and is lowered gradually. Metals deposit at 0.00084-0.0043 amps/cm^2 (0.006-0.03 amps/in^2) and organics at 1/10 of these values. Both pH and additive agents can accelerate or impede deposition; temperature and agitation accelerate deposition; and ultrasonics may speed impurity deposition.

While a comprehensive review of purification techniques is beyond the scope of this report, the above summary indicates some of the types of treatment available to the plater. The effect of impurities on plating characteristics should be studied in pilot-scale and full-scale operations for each bath, and purification techniques should be recommended on a case-by-case basis.

SECTION IV
EXPERIMENTAL

SCOPE OF EXPERIMENTS

The scope of the experimental study is summarized in Table 4. A total of nine different plating baths were studied. Bath solutions were obtained from actual in-field plating operations. Chromium and cyanides were of particular interest because of their high-volume usage in the industry. Bath properties (total dissolved solids and pH) are listed in Table 4. Also shown are the concentration and pH ranges for the test solutions, prepared by diluting the bath samples with deionized water. Three commercially available modules were tested:

1. A duPont B-9 hollow-fiber module containing a polyamide membrane (E.I. DuPont de Nemours and Co., Inc., Permasep Products, Wilmington, Delaware, 19898).
2. A T.J. Engineering 97H32 spiral-wound module containing a cellulose acetate membrane (T.J. Engineering, Inc., Downey, Cal.).
3. An Abcor TM5-14 tubular module containing a cellulose acetate membrane (Abcor, Inc., 341 Vassar St., Cambridge, Massachusetts, 02139).

Because of the pH limitations of the cellulose acetate membrane, only the polyamide membrane (duPont hollow-fiber module) was used in tests with cyanide solutions.

Two types of tests are required in order to assess the ability of RO to treat a specific plating waste. First, short-term tests are required to determine intrinsic membrane performance, and second, long-term life tests are required to determine the stability of performance over long periods.

Table 4. Summary of Experiments

Baths				Properties of Test Solutions		Membrane Modules Tested*
Plating Baths	Source of Bath	Properties of Bath		Concentration Range(TDS-mg/l)	pH Range	
		TDS-mg/l	pH			
Chromic Acid (Neutralized)	Whyco Chromium Company	37.1	--	0.3 - 15.0	5.3 - 6.4	A, B, C
Chromic Acid (Unneutralized)	Whyco Chromium Company	27.5	0.53	0.4 - 9.0	0.9 - 1.9	A, B, C
Copper Pyroshosphate	Honeywell (M & T)	31.9	8.8	0.2 - 21.0	7.1 - 8.5	A, B, C
Nickel Sulfamate	Honeywell (Harstan)	31.0	4.2	0.5 - 26.0	4.6 - 6.1	A, B, C
Nickel Fluoborate	Hampden Colors & Chemicals	25.7	3.5	0.9 - 17.0	1.9 - 4.9	A, C
Zinc Chloride	General Electric (Conversion Chemical)	19.8	4.5	0.2 - 12.0	4.7 - 6.1	A, B, C
Cadmium Cyanide	American Electro-plating Co.	26.3	13.1	0.3 - 10.0	11.4 - 12.9	A
Zinc Cyanide	American Electro-plating Co.	11.4	13.9	0.5 - 4.0	12.3 - 13.7	A
Copper Cyanide	American Electro-plating Co.	37.0	13.3	0.6 - 8.0	11.8 - 12.9	A
Rochelle Copper Cyanide	Whyco Chromium Company	12.7	11.2	0.13 - 3.3	9.8 - 10.6	A
Zinc Cyanide Life Test	American Electro-plating Co.	26.3	13.1	0.3 - 10.0	11.4 - 12.9	A

* A - DuPont B-9 permeator, polyamide hollow fiber membrane.
B - T.J. Engineering 97 H 32 spiral wound module; cellulose acetate membrane.
C - Abcor TM 5-14 module, tubular configuration; cellulose acetate membrane.

Short-term tests were conducted with all the wastes listed in Table 4, however, because of the time involved, life tests were conducted with zinc cyanide only.

TEST SYSTEM

A flow schematic for the pilot plan memerane test system used is shown in Figure 5. A feed sample was charged to a 76 liter (20 gallon) surge tank. A level switch served as a safety device to shut down the system if the surge tank contents were depleted. A temperature switch controlled the flow of either hot or cold water through a coil installed in the tank so as to permit operation at the desired test temperature. Feed solution was pumped through a 20-micron cartridge filter by a low-pressure booster pump. The filter solution was then pumped through the membrane modules by a high-pressure positive-displacement pump; a pressure relief valve prevented system overpressurization. Inlet and outlet pressures for the three membrane modules were measured, and the outlet pressures were individually controlled with back pressure regulators. Concentrate and permeate flows were measured before being returned to the surge tank. Samples of the various permeates and concentrates were collected through the sample valves shown.

OPERATING PROCEDURE

The test system was operated in a "differential" mode. Samples were diluted to rinse water concentration in the surge tank and pumped through the membrane elements. Both concentrate and permeate were returned to the surge tank, so that feed concentration was time-invariant. This permitted the evaluation of membrane performance at a constant feed concentration. Different feed concentrations were tested by simply changing the dilution of the bath sample. During all tests, operation proceeded at fixed conditions for at least one hour, by which time steady state was attained. At that point, membrane capacity (flux) was measured and samples were collected for chemical analyses.

There are a number of process parameters important in influencing performance and costs of a full-scale unit. These important process parameters are; feed concentration, pH, operating pressure, operating temperature, circulation

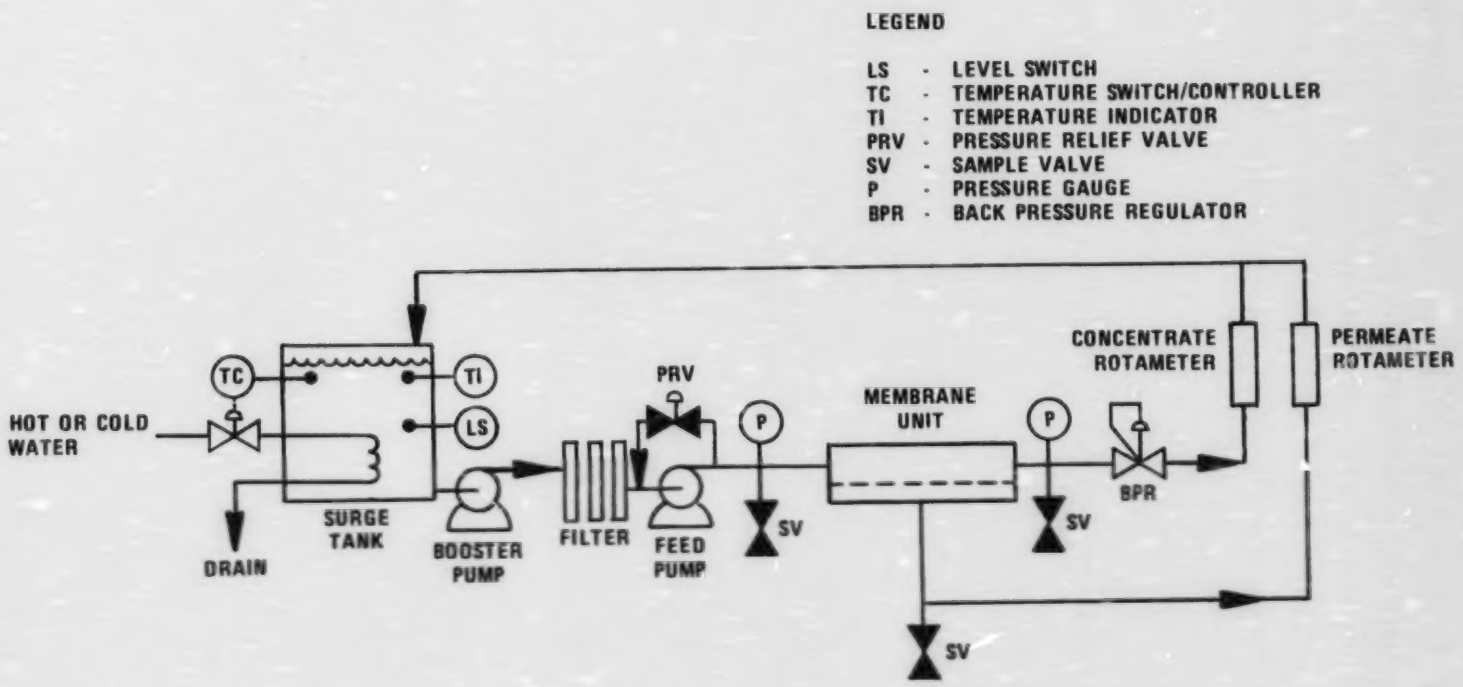

Figure 5. Experimental Apparatus: Flow Schematic

rate, and time over the life of the membrane. The effects of some of these parameters on general membrane performance are well known, and for these (operating pressure, operating temperature, circulation rate, and to some extent pH) optimum conditions have been established. Of the more freely variable parameters, feed concentration, pH, and life times are of greatest interest.

ANALYSES

The methods of analysis used are listed in Table 5. All are from reference 11.

Table 5. Chemical Analyses

Constituent	Method	Procedure (Reference No. 11)
Cadmium	Atomic absorption	129
Total chrome	Atomic absorption	129
Hexavalent chrome	Colorimetric	211-IID
Copper	Atomic absorption	129
Nickel	Atomic absorption	129
Zinc	Atomic absorption	129
Bromide	Colorimetric	108
Chloride	Hg $(NO_3)_2$ Titration	112B
Pyrophosphate	Colorimetric	223
Cyanide	Titration method	207B
Boric acid	As Boron; Semi Colorimetric	107A
Total organic carbon	Combustion-infrared	138A
Total dissolved solids	Gravimetric	148B

SECTION V
RESULTS AND DISCUSSION

GENERAL

Results are presented and discussed below for each system tested. In the short-term tests, the independent variable was the feed concentration, and the dependent variables were the flux and rejection. Flux is reported in terms of gallons per square foot of membrane surface per day (gfd) for the tubular and spiral-wound modules and in terms of gallons per minute per module for the hollow-fiber module. Rejections are plotted as the logarithm of (100-R) in order to clarify the rejection behavior at low feed concentrations. The data are summarized in Tables 6 through 16 and Figures 6 through 50. It should be noted that the use of the high-pressure B-10 hollow fiber module (which was not available at the time of these tests) would give substantially higher fluxes and rejections than reported here for the lower-pressure B-9 module.

In general, operating conditions were held approximately constant. The hollow fiber and spiral wound modules were operated at their pressure limit (29.1 and 43.2 kg/cm^2 [400 and 600 psi] respectively) while the tubular module was operated at 48.6 to 58.2 kg/cm^2 (650 to 800 psi), considerably below its limit of 106 kg/cm^2 (1500 psi). Operation of the tubular module at higher pressures would give higher fluxes and higher rejections than observed in this study.

The feed temperature was maintained at approximately 30°C (86°F). In general, flux increases with temperature at about 3.5% per degree C, but rejection remains essentially independent of temperature. A maximum temperature of 35°C (95°F) is recommended for the duPont polyamide membrane, and a temperature of about 30°C (85°F) is recommended for the cellulose acetate membrane, although

higher tempertures can be tolerated at the expense of a more rapid irreversible loss of flux because of membrane compaction.

The conversion, defined as the ratio of permeate flow to feed flow, is also an important operating variable. When the conversion is low, the entire module "sees" approximately the same concentration, i.e., the feed concentration. However, for high conversions, the average concentration within the module can be considerably greater than the feed concentration. Since both flux and rejection decrease with increasing feed concentration, a module operated under conditions of high conversion is subjected to more severe conditions than a module operated under low-conversion conditions.

The range of conversions differed for the three modules: Tubular, 0-10%; Spiral, 1-30%; Hollow Fiber, 5-75%. Ideally, the flux and rejection should be measured at 0% conversion so the measured flux and rejection will correspond to the known feed concentration rather than to some unknown average concentration. For conversions in the 0-30% range, the measured flux and rejection as a function of feed concentration will be reasonably accurate and in any case conservative (low) compared to the case for 0% conversion. In the range of 5-75% conversion for the hollow fiber module, measurement of the flux and rejection for a given feed concentration may be quite conservative (low) as compared to a measurement at 0% conversion. This is because at 75% conversion, the average concentration seen by the module is on the order of two times the feed concentration.

In general, higher conversions were employed at low feed concentrations. Experimentally, the feed to a module was held constant, and at low feed concentrations, the high flux resulted in high conversions. Conversely, at high feed concentrations the conversion was low, and the concentration dependence of flux and rejection are given more accurately. Therefore, the effect of conversion on the flux and rejection data is: the results are conservative at low feed concentrations and more accurate at higher feed concentrations.

Several trends in the data are obvious. First, the flux decreases with increasing feed concentration. This behavior follows equation (1) since an

increase in feed concentration is accompanied by an increase in osmotic pressure, and the driving force for permeation ($\Delta P - \Delta \Pi$) is reduced. Second, the rejection also generally decreased with increasing feed concentration. This is because the flux of the solute increases with feed concentration, but the flux of water decreases with increasing feed concentration. In many cases, e.g., Figure 8, the rejection decreased at low concentrations. This is attributed to dissociation, at low concentration, of higher molecular weight complexes into lower molecular weight ionic species, for which the membrane rejection is lower.

CHROMIC ACID BATH (NEUTRALIZED)

Neutralization of chromic acid bath rinse waters was found necessary in order to prevent the eventual destruction, by hydrolysis, of the membrane material for all three modules tested. This neutralization was accomplished by addition of NaOH to give a pH of 4.5 to 6, and resulted in a significant extension of membrane life. This pH range was chosen because the rate of hydrolysis of cellulose acetate membranes is at a minimum when the pH value is near 5. Operation at the very low pH values of the unneutralized samples is known to considerably shorten the life of both membranes tested. The question of membrane life is a crucial one, and will be discussed subsequently.

All three membrane modules performed satisfactorily in neutralized chromic acid rinse waters with respect to flux and rejection (see Table 6). Flux decreased with increasing feed concentration as expected, according to the theoretical treatment presented above. This decrease was most pronounced for the hollow-fiber module, since the operating pressure was only 29.1 kg/cm^2 (400 psig) as compared to 43.2 kg/cm^2 and 48.6 kg/cm^2 (600 and 650 psig) for the spiral wound and tubular modules respectively. The decrease in flux is shown graphically in Figures 6 and 7. Note that these pressures were the maximum operating pressures for all but the tubular module, which would have shown significantly improved performance if pressure were increased toward the 106 kg/cm^2 (1500 psig) limit. Flux was good up to about 10% of plating bath concentration (5.4% TDS) and acceptable up to approximately 25% of bath concentration (12.5% TDS). Note in this regard that the particular bath sample chosen for study is of much higher solids content (450 g/l CrO_3) than typical. Thus,

Table 6. Experiment # 1 Chrome Bath
(Neutralized with NaOH)

Feed Solution		Membrane Module	Operating Conditions			Flux (gfd)	% Rejection	
% Solids(1,3)	% Bath(2,4)		Pressure (psi)	Temperature (°C)	PH of Feed		Total Dissolved Solids	Cr^{+6}
.28	.57	Hollow Fiber	400	20	6.1	3.02	97.9	99.4
		Spiral	600			14.0	95.1	94.8
		Tubular	650			10.4	96.7	97.5
1.55	2.91	Hollow Fiber	400	30	4.5	2.26	98.8	97.4
		Spiral	600			11.6	95.7	96.2
		Tubular	650			7.12	97.9	98.6
2.70	5.16	Hollow Fiber	400	39	4.7	1.68	98.7	97.6
		Spiral	600			9.01	96.1	96.0
		Tubular	650			6.33	97.5	97.4
4.50	9.5	Hollow Fiber	400	28	5.5	1.10	97.6	95.0
		Spiral	600			4.62	90.8	90.8
		Tubular	650			3.96	96.4	96.7
14.9	28.4	Hollow Fiber	400	29	4.4	0.46	40.2	51.7
		Spiral	600			4.23	76.7	76.7
		Tubular	650			0.96	89.2	94.8
37.0	100							

(1) % Total Dissolved Solids (TDS)
(2) % of Plating Bath TDS Concentration
(3) Includes NaOH added
(4) Excludes NaOH added

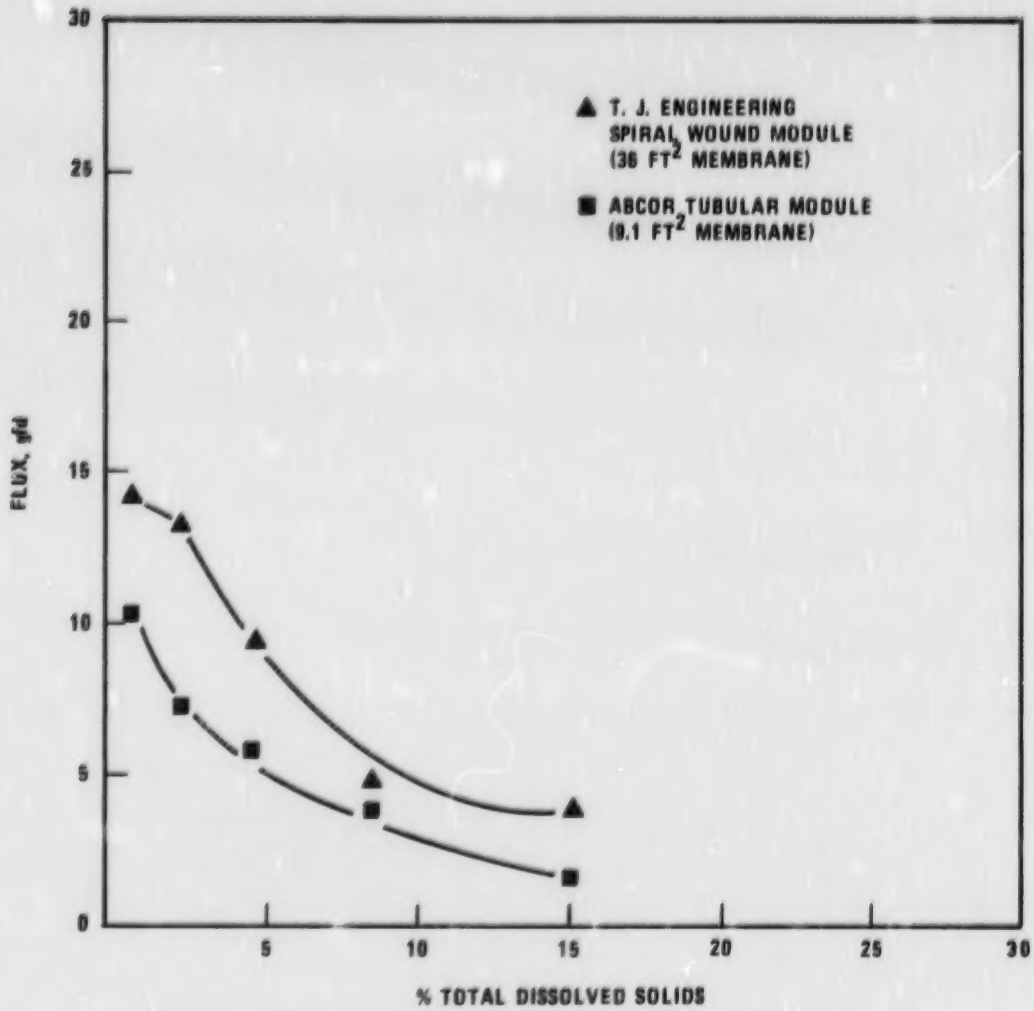

Figure 6. Flux in Neutralized Chrome Bath

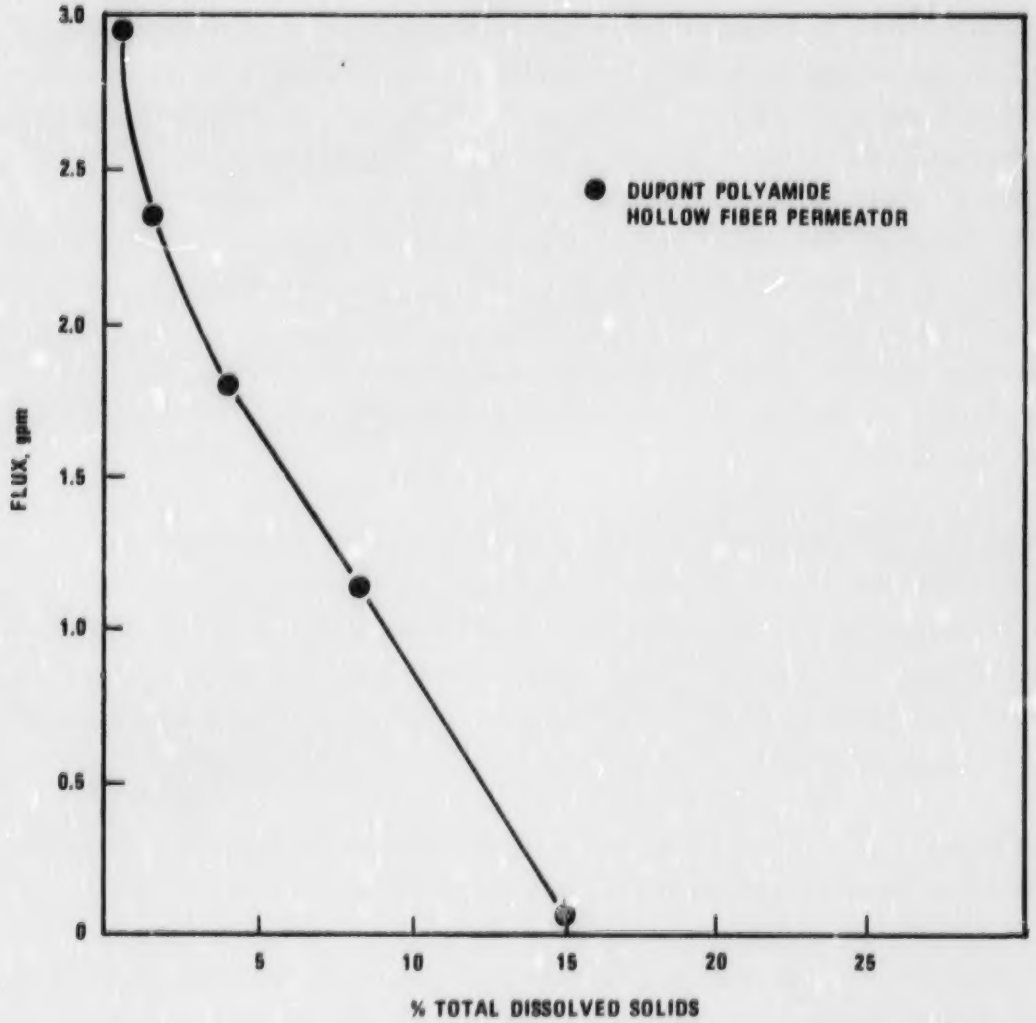

Figure 7. Flux in Neutralized Chrome Bath

flux and rejection results corresponding to 25% of this bath strength are typical of rinse waters of 60 to 75% of normal bath strength.

The quality of the permeate is illustrated in Figure 8 which shows rejection as a function of feed solute concentration for the three membrane systems. These data are based on measurements of the percentage total solids content of the various samples. The corresponding data based on percentage hexavalent chromium content are given in Figure 9. At low to moderately high concentrations (up to 10% of actual bath concentration) rejections were excellent (> 97%). At 25% of actual bath concentrations, rejections were good (> 90%). Only at the sample concentration of 50% of bath concentration did rejection fall to low values. This fall, at the higher feed solute concentrations, was due to the build-up of very high concentrations of solute just at the membrane surface. This build-up was much greater for the higher feed solute concentrations, and the net effect is that greater amounts of solute were permeated.

Note that the rejections for the tubular and spiral wound system increased with concentration at low concentrations before falling at high concentrations. This is believed due to the formation of the larger and more easily rejectable dichromate ion, the formation of which is favored under low acidity/high chromate concentration conditions. Under highly acidic conditions, the formation of chromic acid is favored.

Based on flux and rejection data, reverse osmosis (RO) appears to be an attractive method for concentrating chromium plating bath rinse waters to obtain a concentrate containing about 7 to 9% TDS, if neutralization is practiced. However, the costs of neutralization (equipment and chemicals) and of a process to remove added chemicals, if reuse of the chromic acid is desired (ion exchange), are significant. The development of an oxidant resistant membrane, which could be used to concentrate chromic acid rinse waters without neutralization, is clearly desirable. The availability of such a membrane would likely result in widespread use of RO for concentrating chromium rinses.

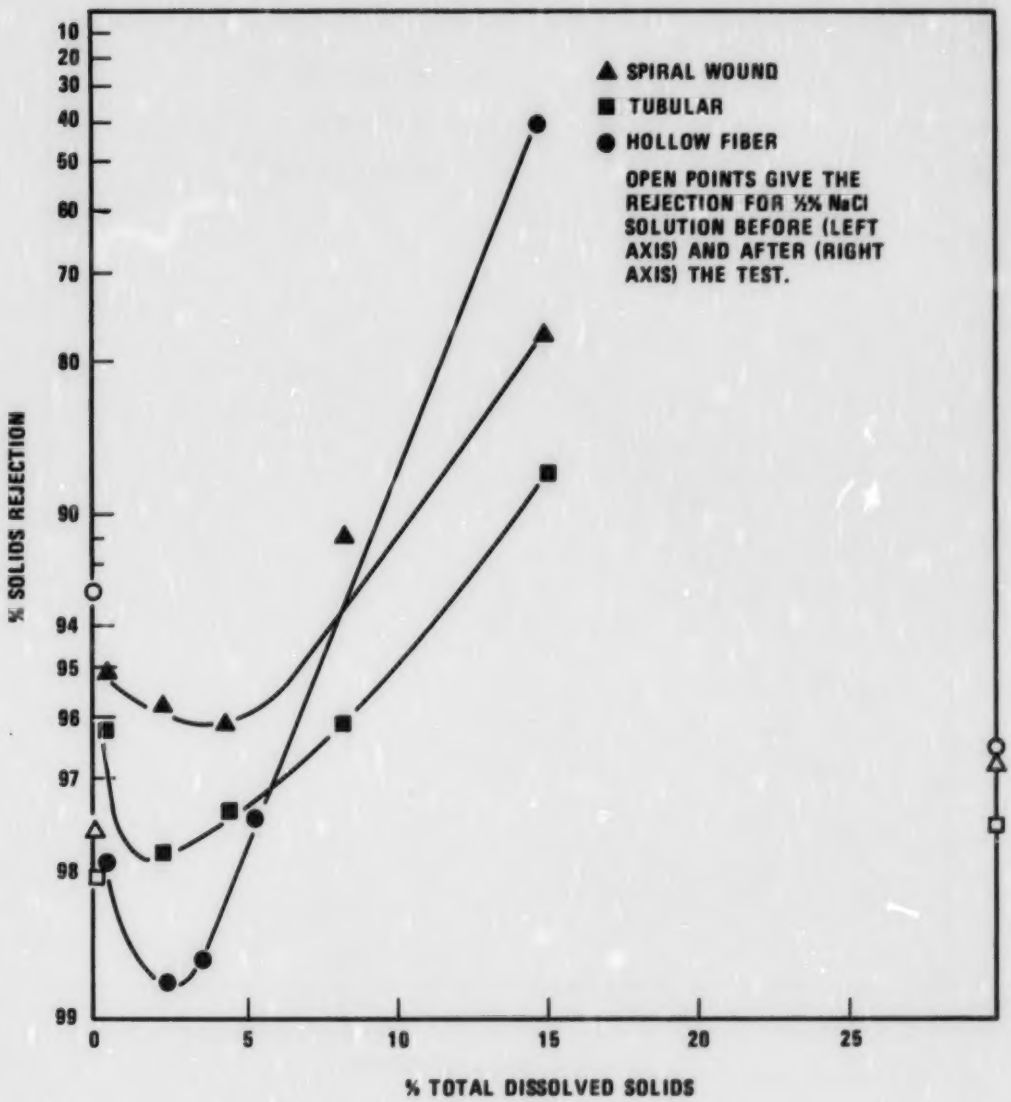

Figure 8. Solids Rejection in Neutralized Chrome Bath

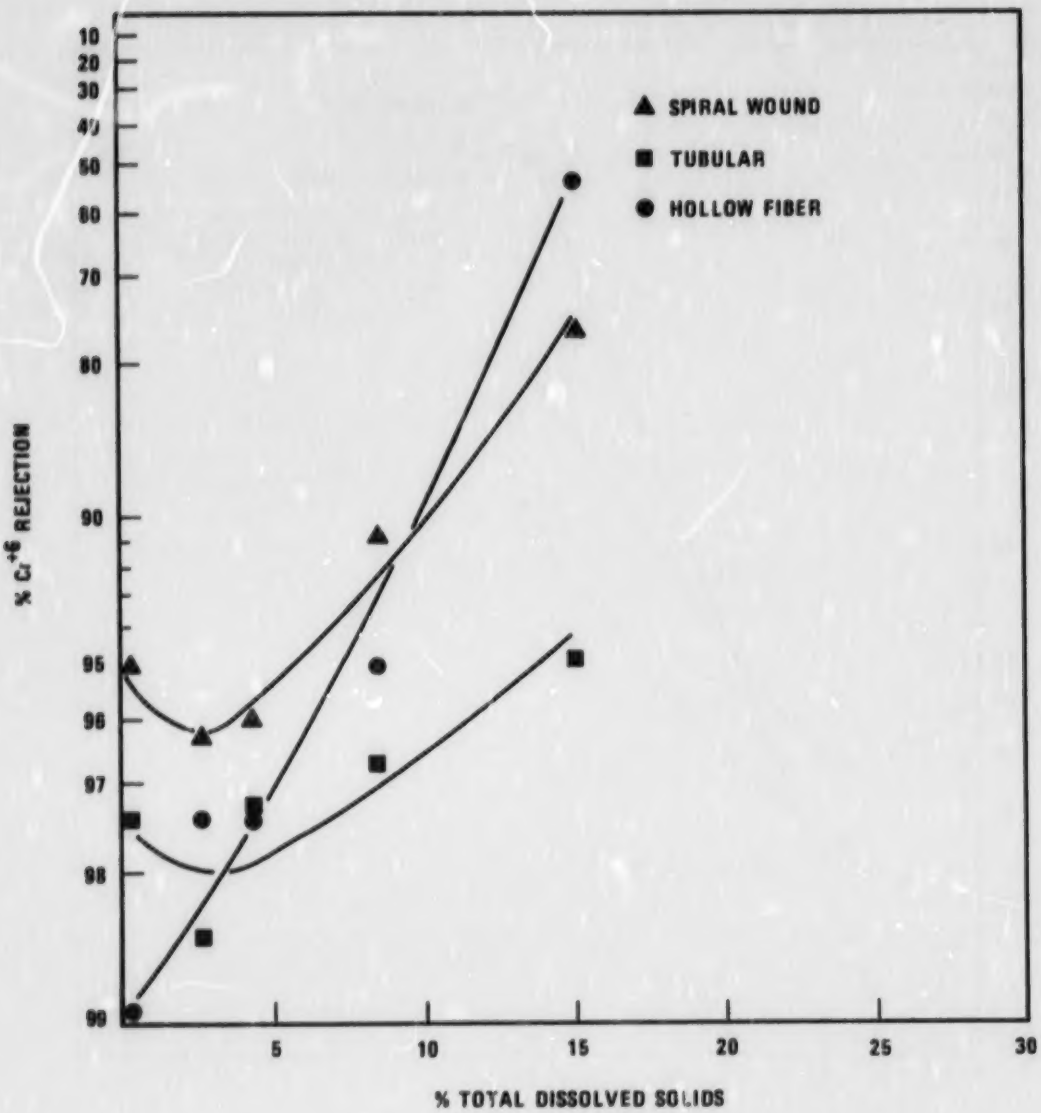

Figure 9. Cr^{+6} Rejection in Neutralized Chrome Bath

CHROMIC ACID BATH (UNNEUTRALIZED)

The flux and rejection results (Table 7) for the unneutralized chromic acid rinse waters were similar to those for the neutralized chromic acid rinse waters, as is evident from Figures 10 and 11 (flux data), Figure 12 (rejection data based on TDS) and Figure 13 (rejection data based on Cr^{+6}). The maximum in the rejection behavior was apparently absent, suggesting that dichromate formation is inhibited in low pH samples. Because of the hydrolysis and eventual destruction of the membranes tested with unneutralized samples, these results are only of interest for the indication that RO will be effective if suitable hydrolysis-resistant membranes can be formulated.

COPPER PYROPHOSPHATE

Permeate fluxes and rejections were, for the most part, very favorable for this system (see Table 8). As is seen in Figures 14 and 15, flux was excellent for the tubular module up to the highest feed concentration tested (approximately 40% of bath concentration) and excellent for the spiral wound module up to approximately 25% of bath concentration (10.5% TDS). Flux was good for the hollow fiber module up to 15 to 20% of bath concentration (7-8% TDS).

Rejection results were also highly favorable, as can be seen in Figures 16, 17, and 18, based on TDS, Cu^{+2}, and $P_2O_7^{-4}$ concentrations, respectively. In particular, rejections for the spiral wound module were excellent up to 25% of bath concentration (10.5% TDS) and good up to approximately 40% of bath concentration (15% TDS). Maximum rejections based on Cu^{+2} and $P_2O_7^{-4}$ were 99.6 and 99.7%, respectively, for this membrane.

The hollow fiber membrane also performed very well. Less attractive was the performance of the tubular membrane. This is unexpected based on the performance of this configuration with other plating bath samples and is believed due to the use of the membrane module in the immediately preceding unneutralized chromic acid tests. The membrane was apparently partially hydrolyzed, as was evident from the rejection of 0.5% NaCl solution at the completion of the copper pyrophosphate experiments. Results comparable to, or better than, the spiral wound membrane would be expected for a fresh tubular membrane.

Table 7. Experiment # 2 Chrome Bath
(Unneutralized)

Feed Solution		Membrane Module	Operating Conditions			Flux (gfd)	% Rejection	
% Solids[1]	% Bath[2]		Pressure (psi)	Temperature (°C)	PH of Feed		Total Dissolved Solids	Cr^{+6}
.398	1.45	Hollow Fiber	400	29	1.9	2.59	84.3	97.0
		Spiral	600			15.3	97.3	95.6
		Tubular	650			10.0	99.4	97.8
1.83	6.65	Hollow Fiber	400	29	1.2	1.97	95.0	86.7
		Spiral	600			13.2	94.0	86.1
		Tubular	650			8.58	96.9	90.6
4.11	14.9	Hollow Fiber	400	29	1.2	1.20	89.9	91.1
		Spiral	600			10.6	91.7	92.2
		Tubular	650			7.31	95.2	95.6
9.43	34.3	Hollow Fiber	400	28	0.9	leaks	leaks	leaks
		Spiral	600			leaks	leaks	leaks
		Tubular	650			6.60	94.2	97.0

(1), (2) See Table 6

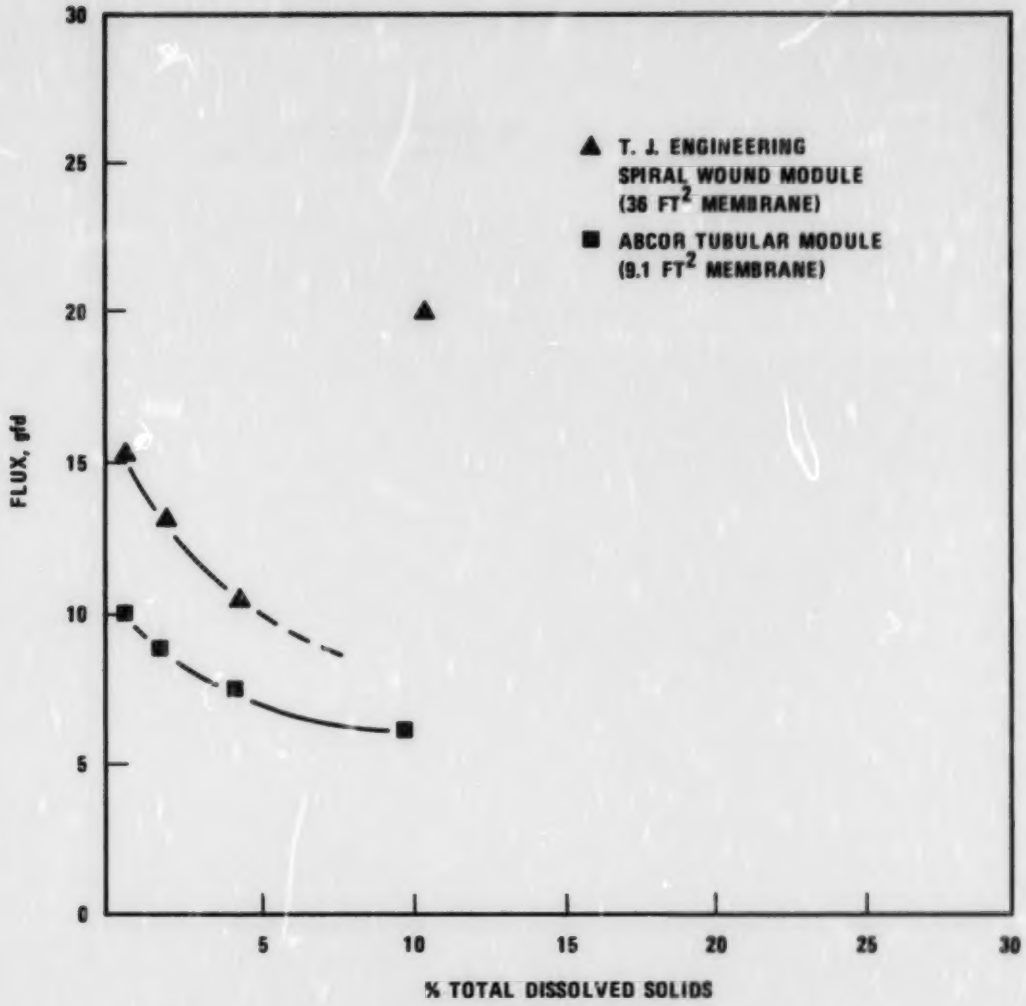

Figure 10. Flux in Unneutralized Chrome Bath

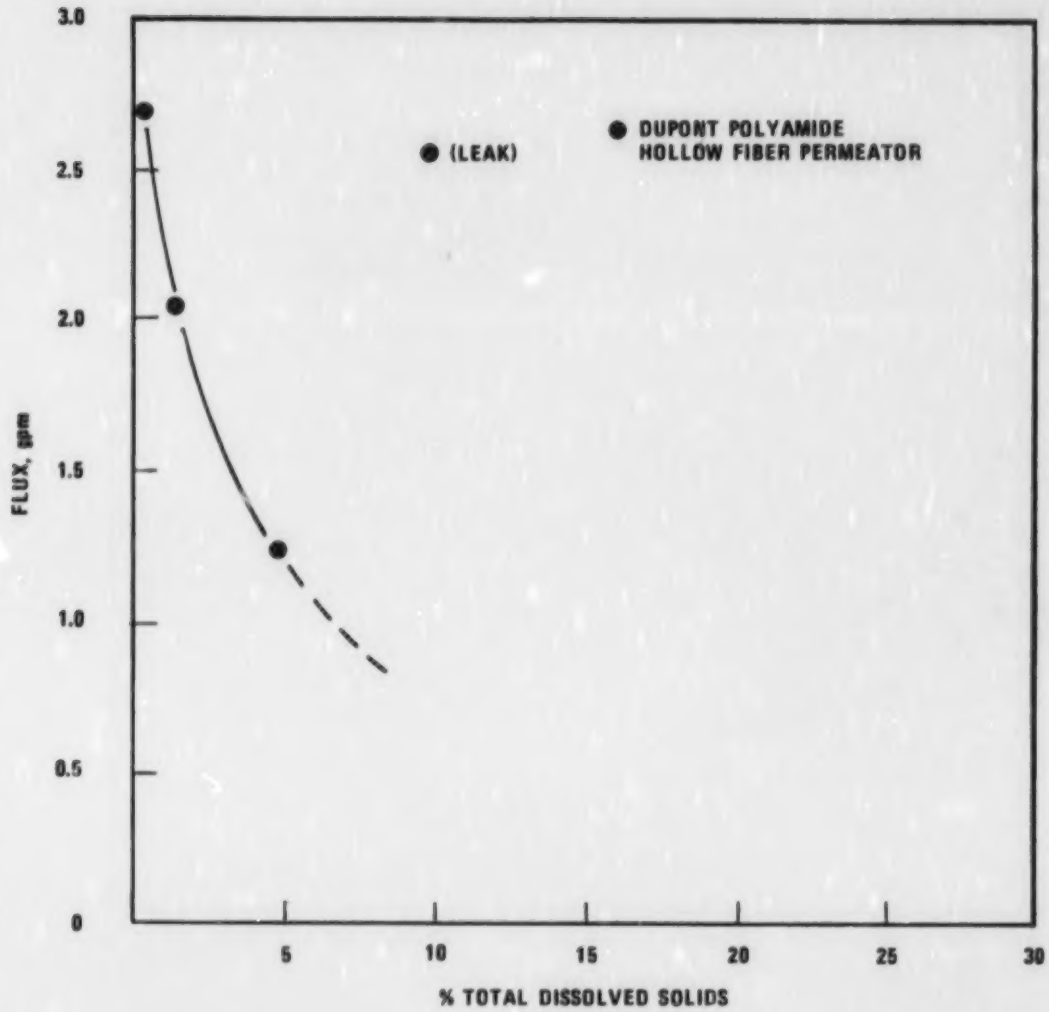

Figure 11. Flux in Unneutralized Chrome Bath

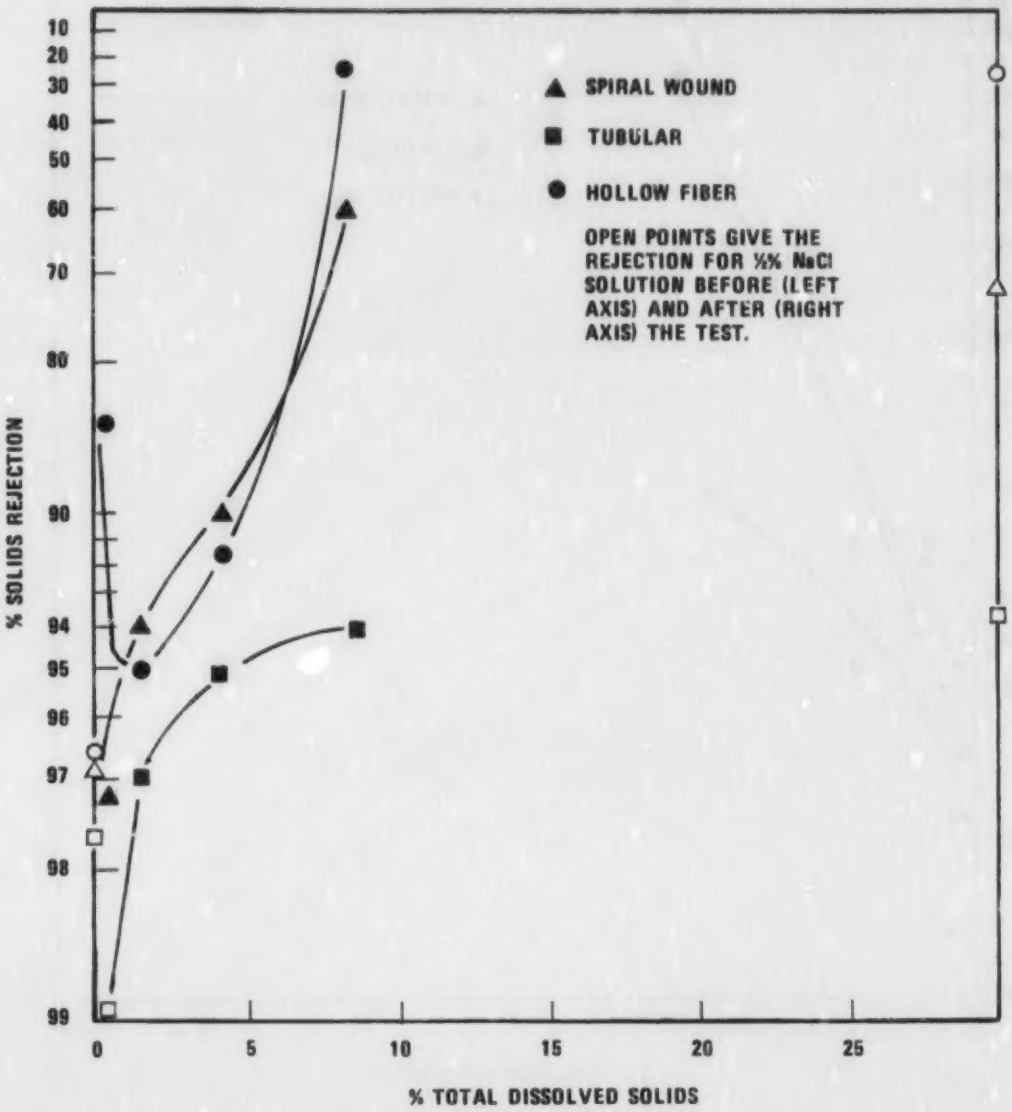

Figure 12. Solids Rejection in Unneutralized Chrome Bath

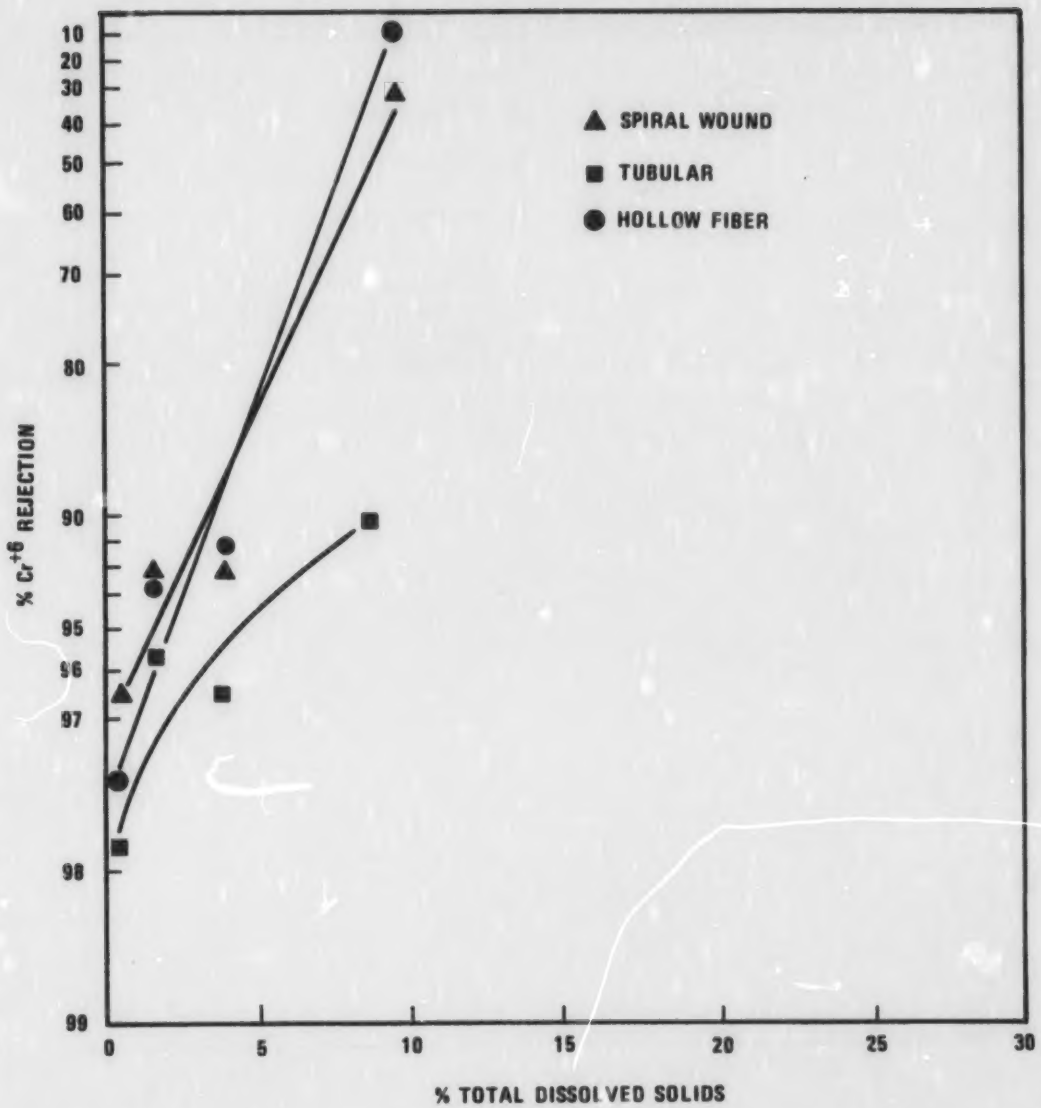

Figure 13. Cr^{+6} Rejection in Unneutralized Chrome Bath

Table 8. Experiment # 3 Copper Pyrophosphate Bath

Feed Solutions		Membrane Module	Operating Conditions			Flux (gfd)	% Rejection		
% Solids[1]	% Bath[2]		Pressure (psi)	Temperature (°C)	pH of Feed		Total Dissolved Solids	Cu^{+2}	$P_2O_7^{-4}$
.177	.55	Hollow Fiber	400	28	6.8	2.88	92.4	99.8	98.1
		Spiral	600			21.7	91.2	99.5	99.1
		Tubular	800			26.8	97.9	≈100	≈100
1.09	3.42	Hollow Fiber	400	31	7.0	2.45	98.5	99.9	99.6
		Spiral	600			18.2	97.8	99.6	99.7
		Tubular	800			20.9	98.8	99.7	99.7
2.47	7.74	Hollow Fiber	400	29	7.3	2.11	99.0	99.6	99.7
		Spiral	600			16.7	98.0	99.6	99.6
		Tubular	800			18.0	97.2	99.3	99.4
5.22	16.4	Hollow Fiber	400	30	7.3	1.34	98.8	99.8	99.5
		Spiral	600			13.4	96.8	99.3	99.4
		Tubular	800			16.5	95.7	98.3	98.6
8.49	26.6	Hollow Fiber	400	30	8.0	.64	93.1	96.0	96.4
		Spiral	600			10.3	96.7	98.7	98.9
		Tubular	800			13.8	82.5	97.7	98.7
11.4	35.1	Hollow Fiber	400	31	8.5	.088	86.8	87.9	91.2
		Spiral	600			7.4	95.8	98.1	98.2
		Tubular	800			leak	leak	leak	leak
14.5	45.5	Hollow Fiber	400	34	8.4	0.016	77.7	83.8	80.9
		Spiral	600			3.8	91.5	85.9	94.3
21.4	67.1	Hollow Fiber	400	28	8.3	0.0061	12.4	23.1	50.9
		Spiral	600			.53	60.4	70.8	51.8

(1), (2) See Table 6

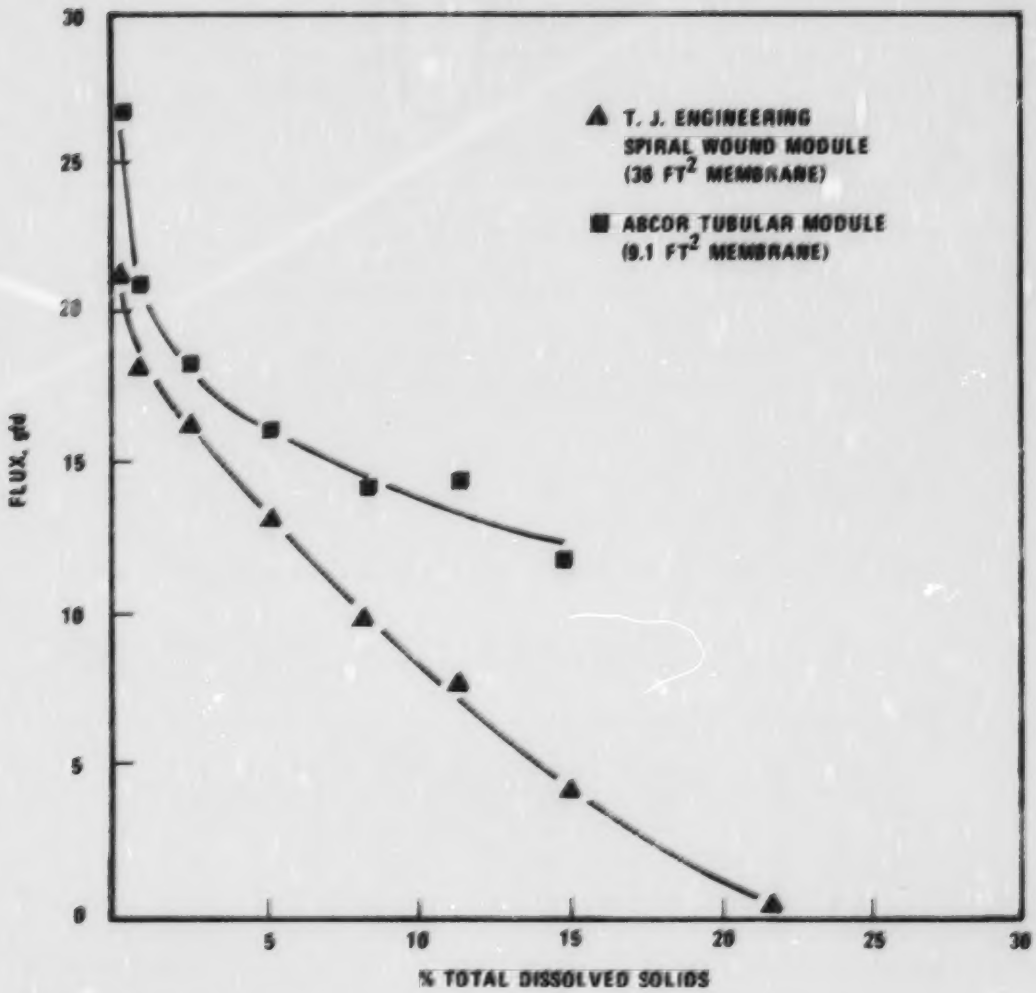

Figure 14. Flux in Copper Pyrophosphate Bath

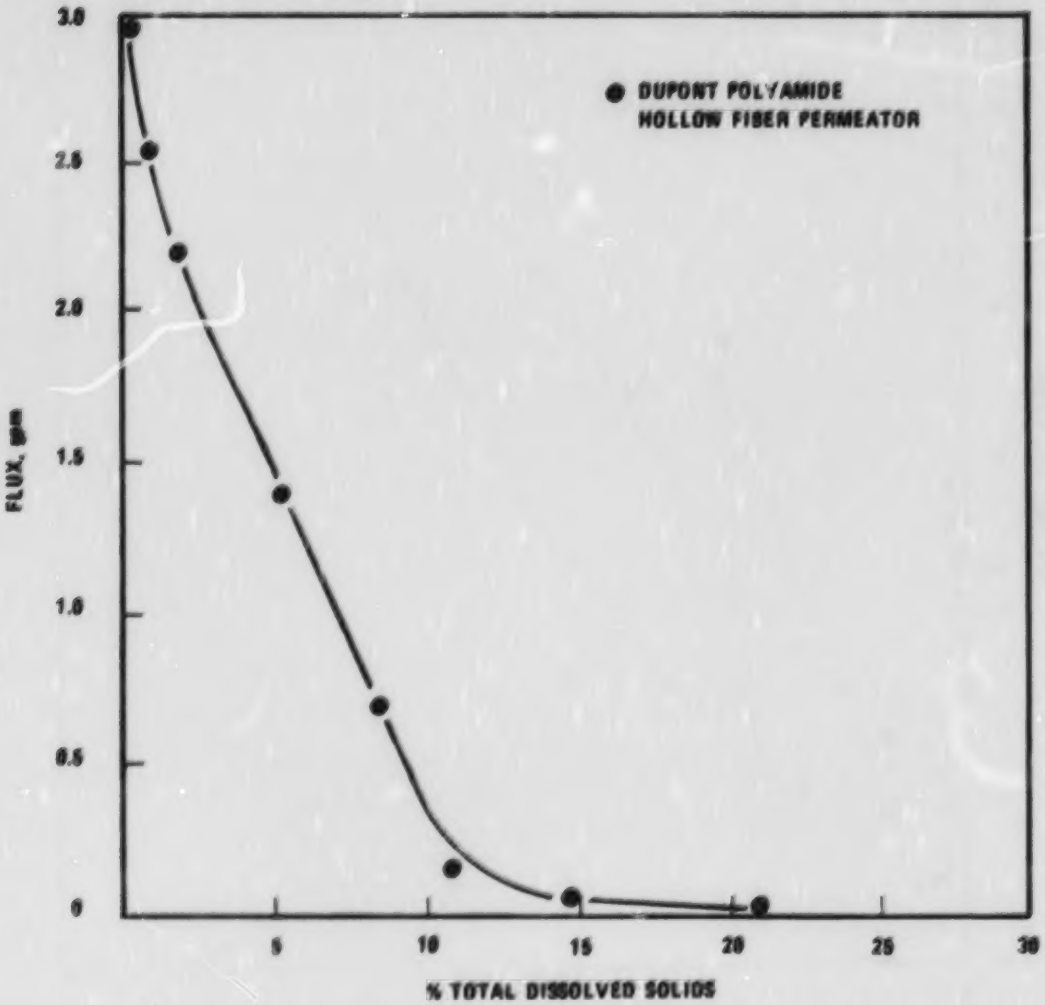

Figure 15. Flux in Copper Pyrophosphate Bath

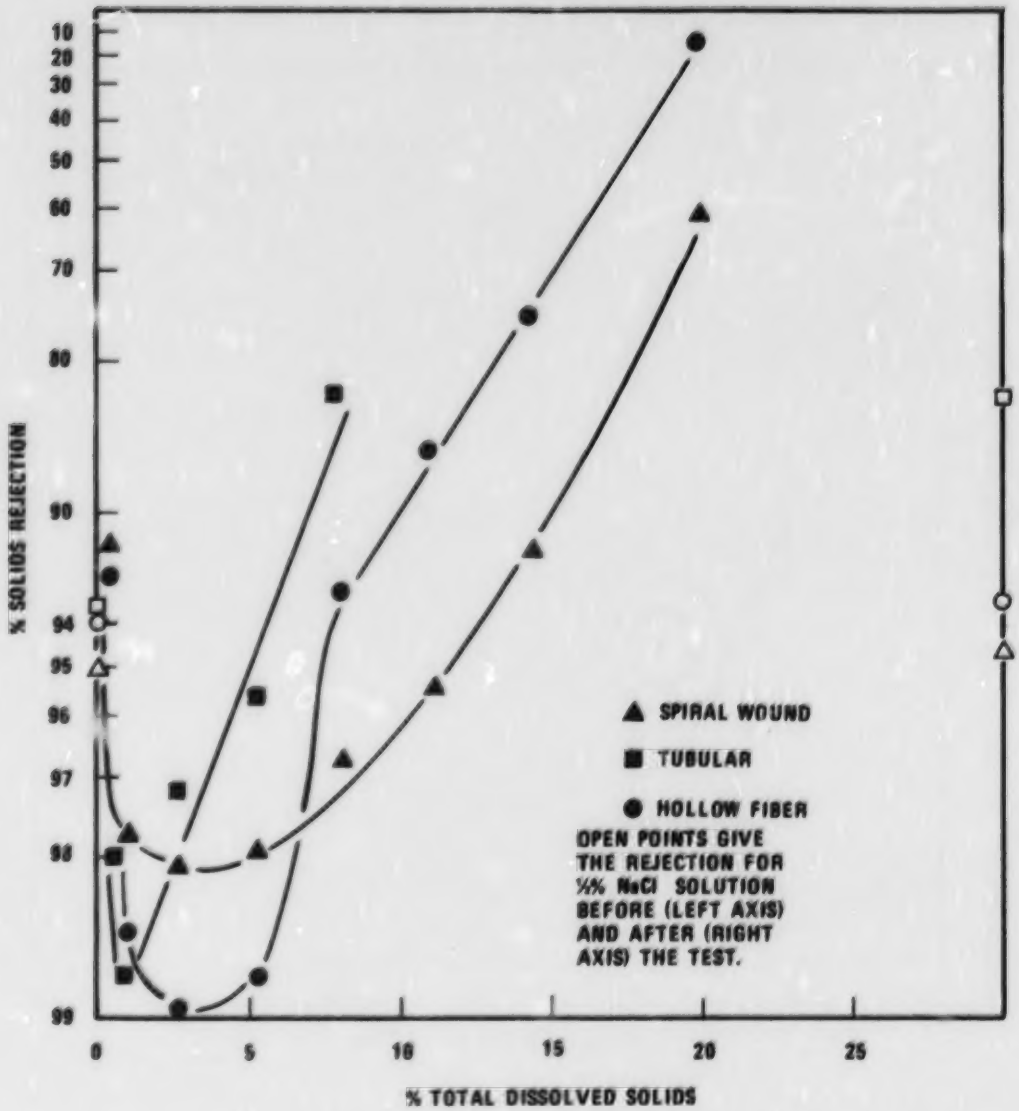

Figure 16. Solids Rejection in Copper Pyrophosphate Bath

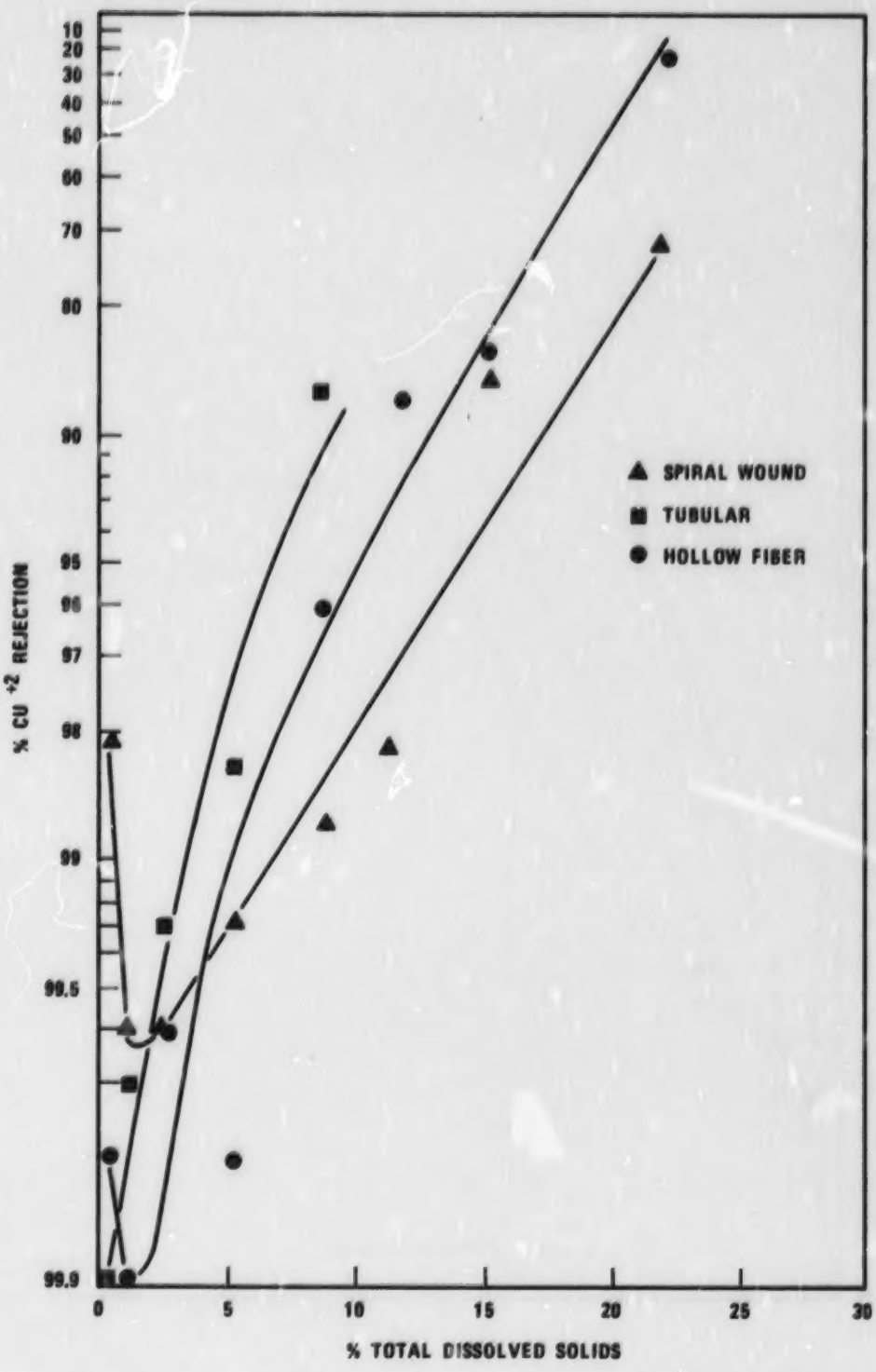

Figure 17. Cu^{+2} Rejection in Copper Pyrophosphate Bath

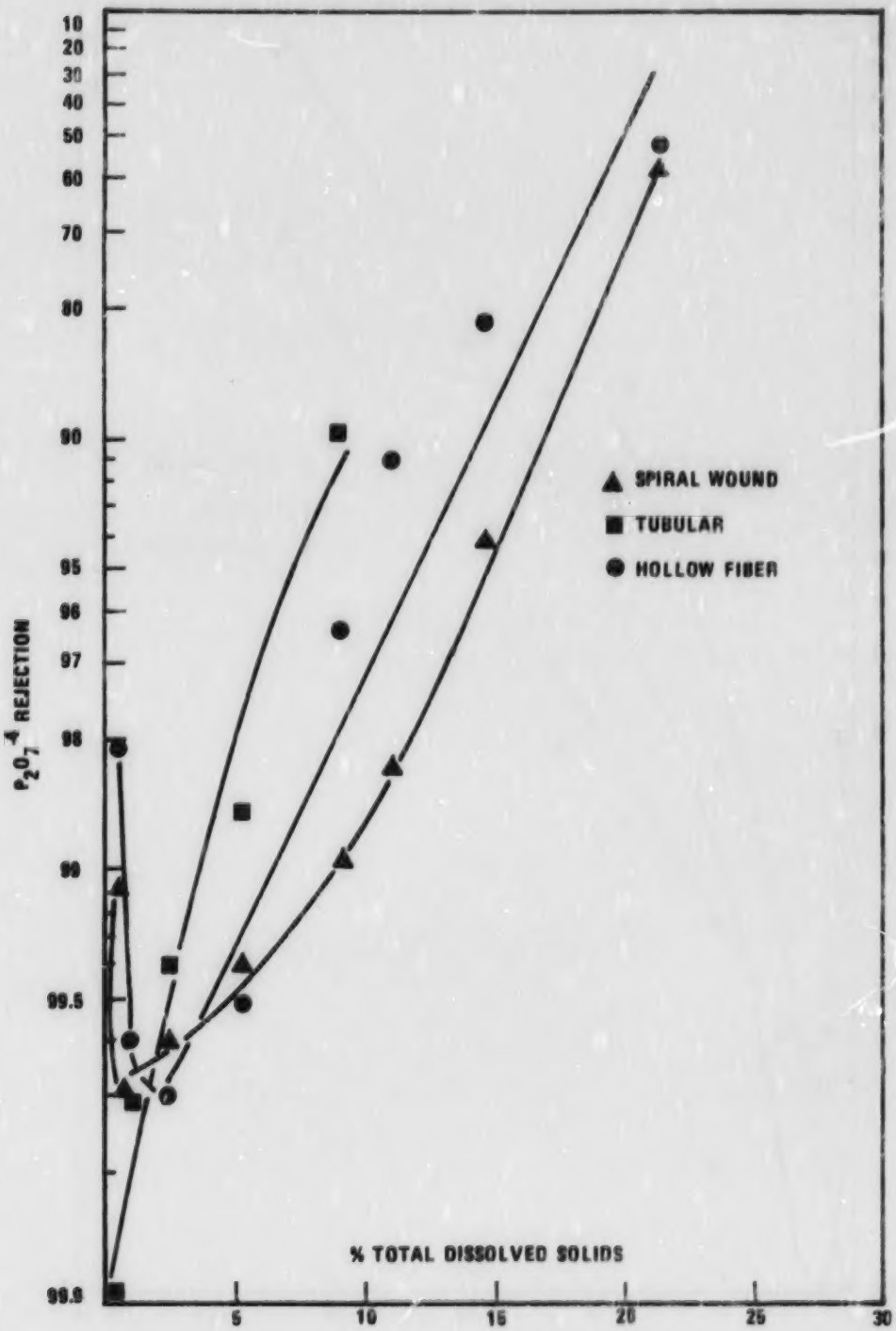

Figure 18. $P_2O_7^{-4}$ Rejection in Copper Pyrophosphate Bath

Based on the flux and rejection results, the copper pyrophosphate system appears to be a most attractive candidate for RO treatment. No pH adjustment would be necessary for operation with any of the three commercially available membranes tested, and no evidence of fouling was observed. One limitation which was not evaluated is the possible conversion of pyrophosphate to orthophosphate, and the effect on bath performance of its build-up in a closed loop system.

NICKEL SULFAMATE

All three membrane modules performed satisfactorily with nickel sulfamate plating bath rinse waters (see Table 9). Flux data are presented in Figure 19 for the spiral wound and tubular modules, and in Figure 20 for the hollow fiber module. Flux was excellent up to 40% of bath concentration (15% TDS) for the tubular module and good nearly to this level for the spiral wound module. Flux was acceptable for the hollow fiber module up to only about 20% of bath concentration.

Rejection results were quite good for all three modules based on concentrations of TDS (Figure 21), Ni^{+2} (Figure 22), Br^{-} (Figure 23), and total organic carbon (Figure 24). Rejection of boric acid was only fair (tubular) to poor (spiral wound and hollow fiber) as seen in Figure 25. In general, there were no distinct differences in rejection performance for the three module types, unlike the behavior for most other systems. Rejections were good up to approximately 15 to 20% of bath composition (7-8% TDS) for all components except total organic carbon, for which they were acceptable, and boric acid, for which they were only fair. Similar behavior has been reported for treatment of Watts Nickel baths.[1.2]

Nickel sulfamate plating bath rinse waters may well be suitable for RO treatment. No pH adjustment would be necessary and rejection results are quite attractive for all modules. Flux results favor the tubular and spiral wound configurations, but an economic study would be needed to make a final determination of membrane configuration. In addition, nickel sulfamate baths are operated at elevated temperatures where evaporation is substantial, and a high

Table 9. Experiment # 4 Nickel Sulfamate Bath

Feed Solutions		Membrane Module	Operating Conditions			Flux (gfd)	% Rejection				
% Solids[1]	% Bath[2]		Pressure (psi)	Temperature (°C)	pH of Feed		Total Dissolved Solids	Ni^{+2}	Br^-	H_3BO_3	TOC
.499	1.60	Hollow Fiber	400	30	6.1	2.02	94.8	93.5	≈100	40.0	96.1
		Spiral	600			17.1	96.8	95.3	≈100	16.7	95.1
		Tubular	800			25.1	91.6	95.4	97.7	66.7	94.2
2.39	7.68	Hollow Fiber	400	30	5.8	1.58	95.8	95.9	99.3	44.3	92.5
		Spiral	600			15.6	93.3	95.6	97.2	13.6	86.0
		Tubular	800			20.9	93.8	95.8	97.0	70.5	98.5
4.11	13.2	Hollow Fiber	400	29	5.5	.96	96.7	97.6	91.2	61.9	91.3
		Spiral	600			12.9	94.6	94.7	95.6	38.1	83.9
		Tubular	800			17.6	90.5	94.8	92.2	55.0	83.4
6.17	19.8	Hollow Fiber	400	29	5.3	.38	92.4	94.8	89.2	5.0	82.8
		Spiral	600			9.83	89.2	92.4	92.5	39.6	73.9
		Tubular	800			15.5	89.6	92.0	89.6	50.5	80.2
12.0	38.6	Hollow Fiber	400	29	4.9	.048	73.9	86.6	39.5	26.3	56.9
		Spiral	600			6.34	90.0	84.1	86.0	35.1	72.5
		Tubular	800			10.9	88.0	90.4	81.8	40.4	70.8
23.6	75.9	Hollow Fiber	400	30	4.6	.015	17.4				9.1
		Spiral	600			.79	51.3				1.5
		Tubular	800			1.67	13.1				1.5

(1), (2) See Table 6

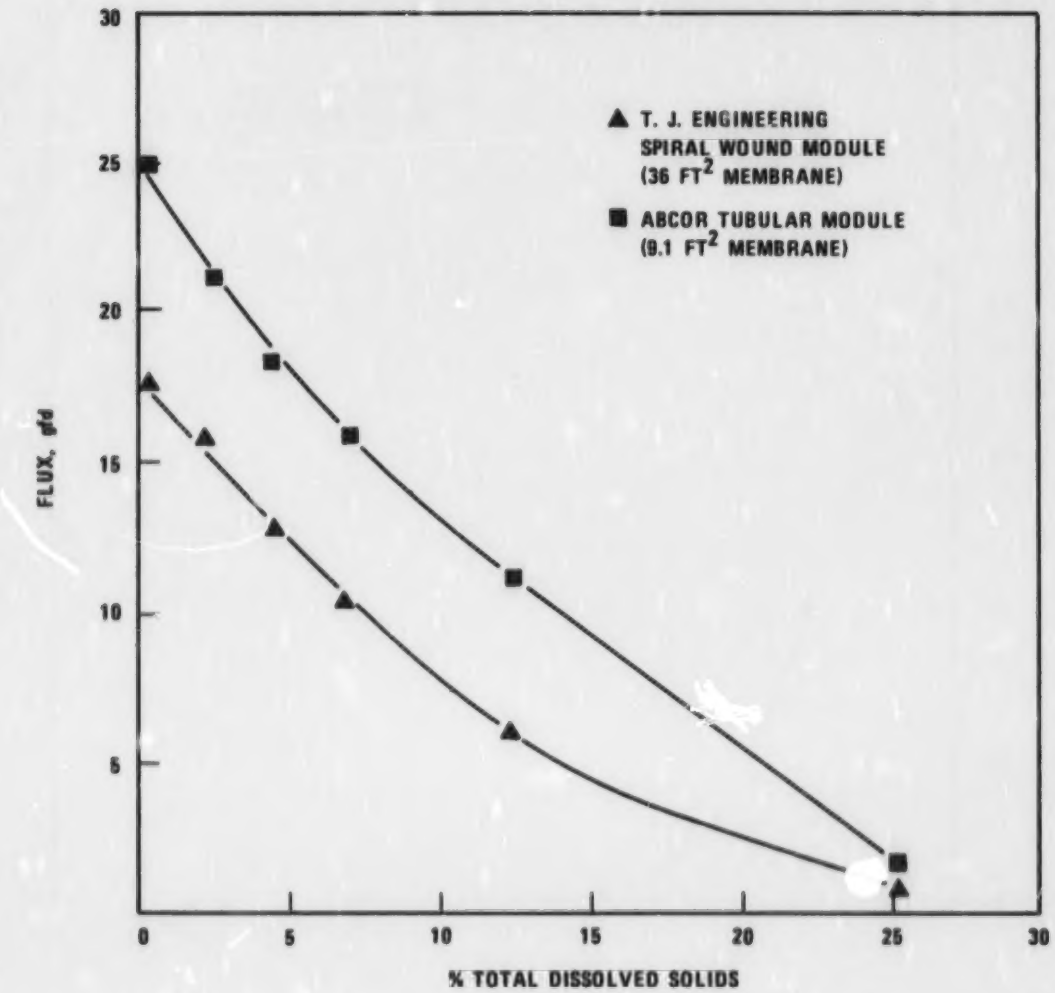

Figure 19. Flux in Nickel Sulfamate Bath

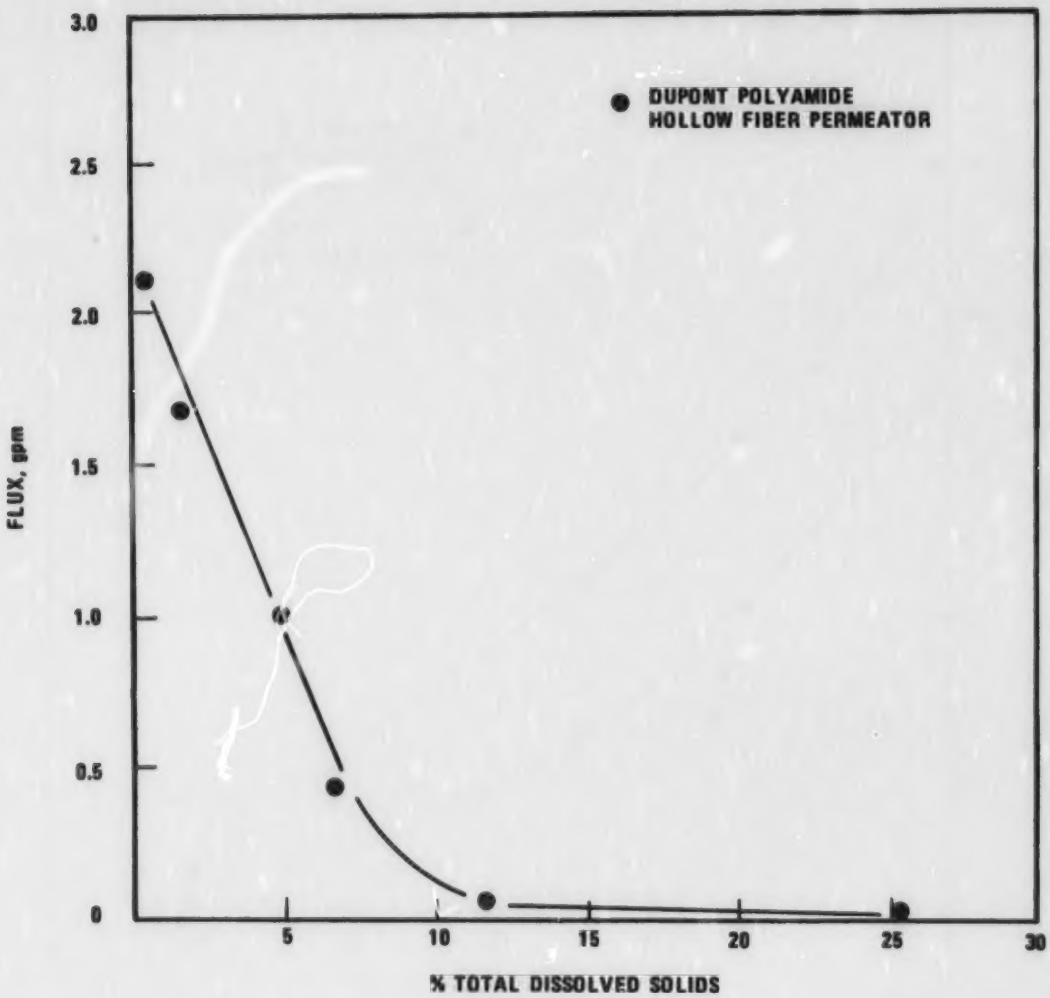

Figure 20. Flux in Nickel Sulfamate Bath

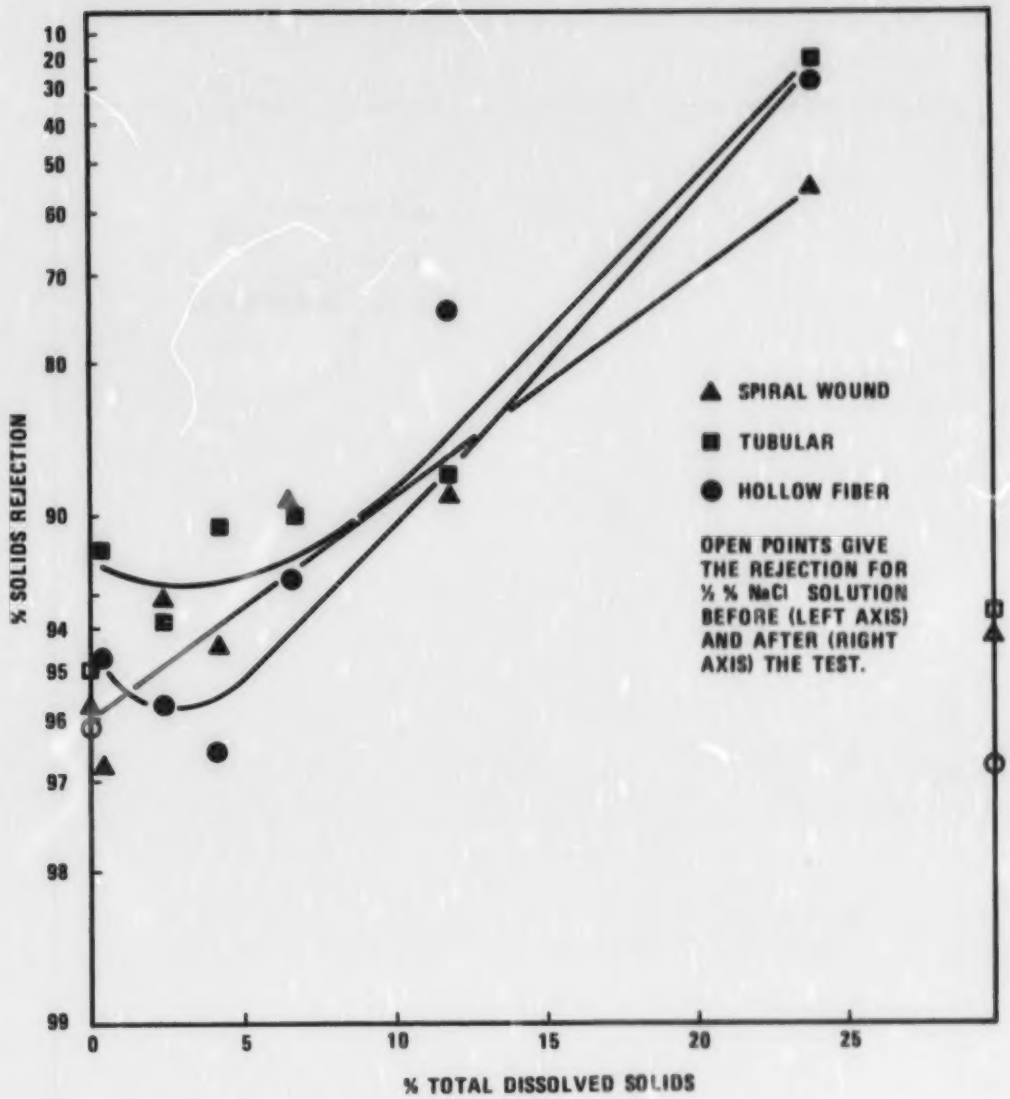

Figure 21. Solids Rejection in Nickel Sulfamate Bath

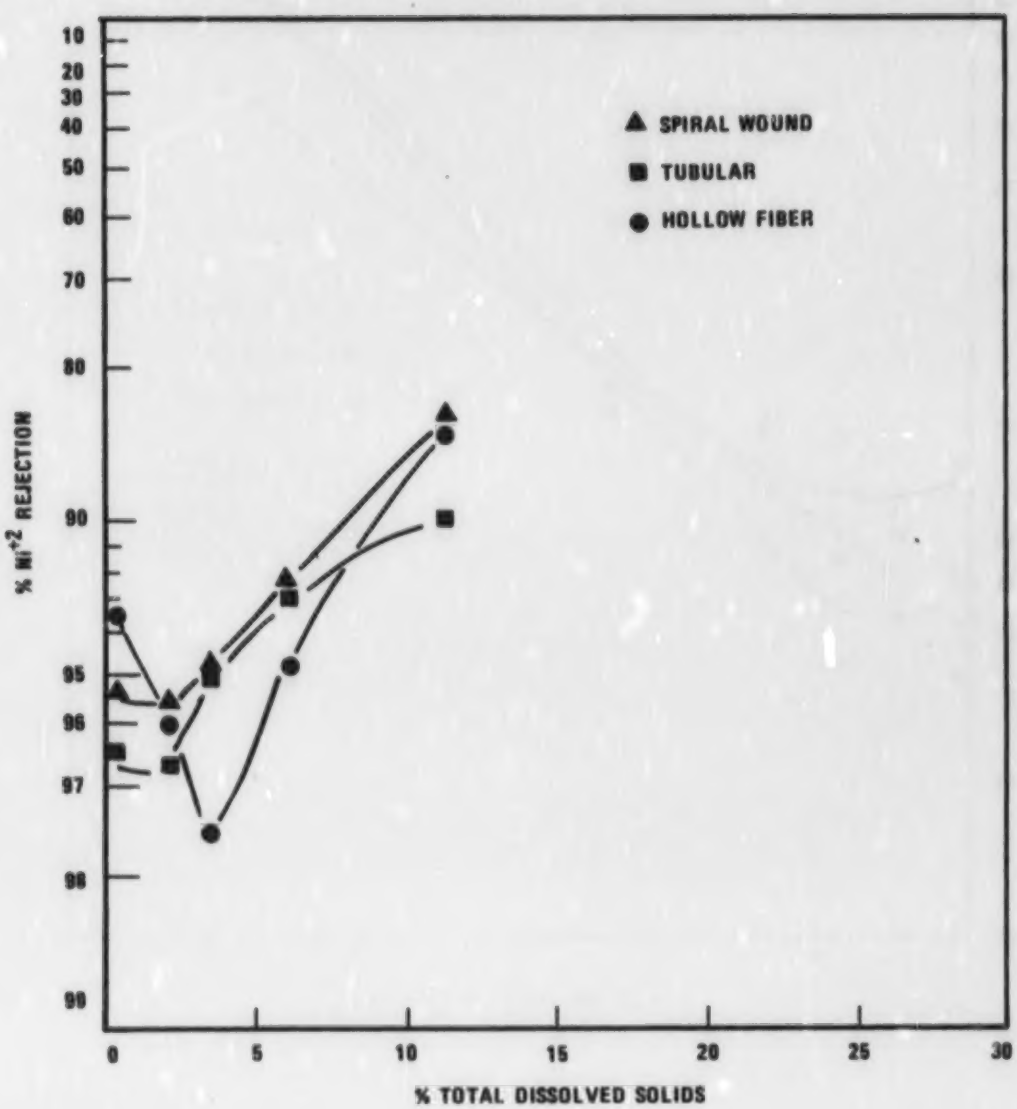

Figure 22. Ni^{+2} Rejection in Nickel Sulfamate Bath

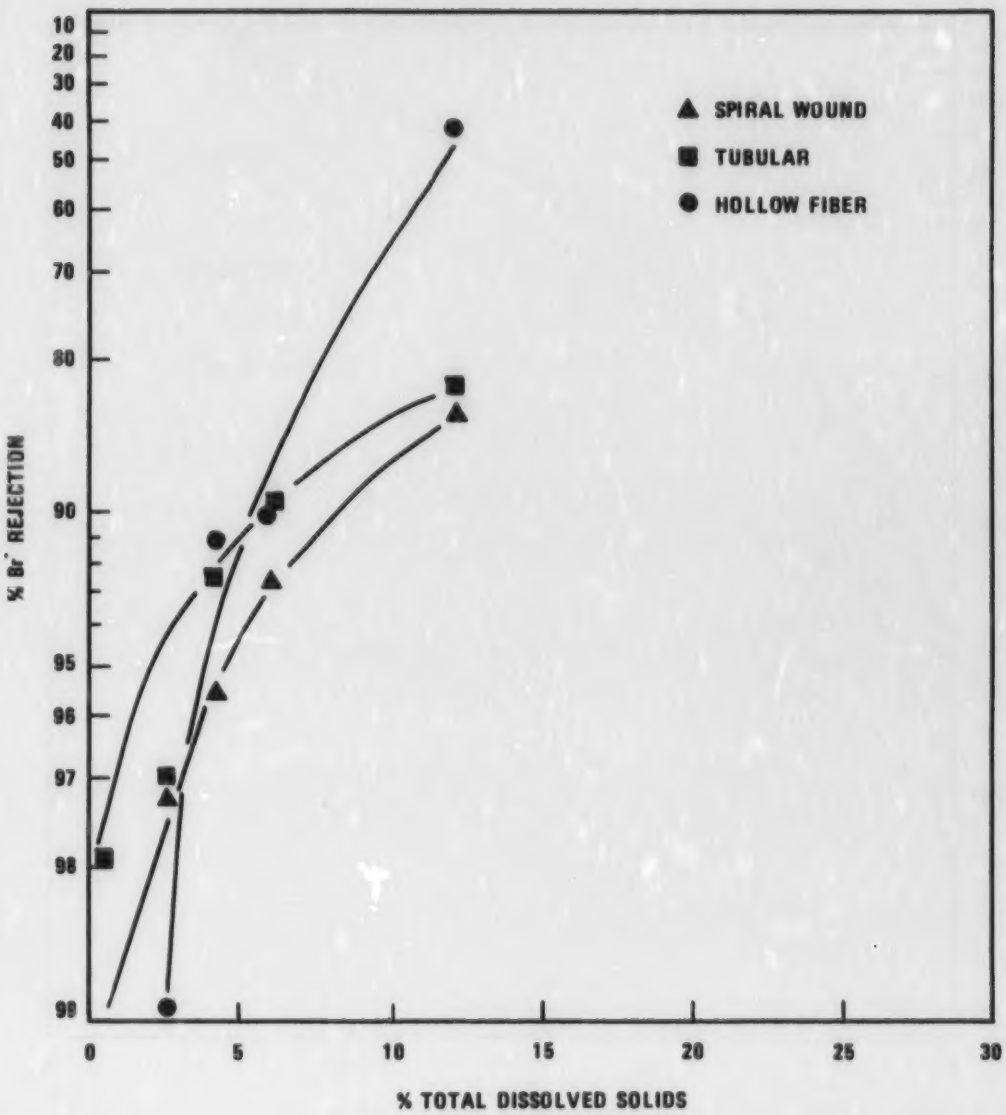

Figure 23. Br^- Rejection in Nickel Sulfamate Bath

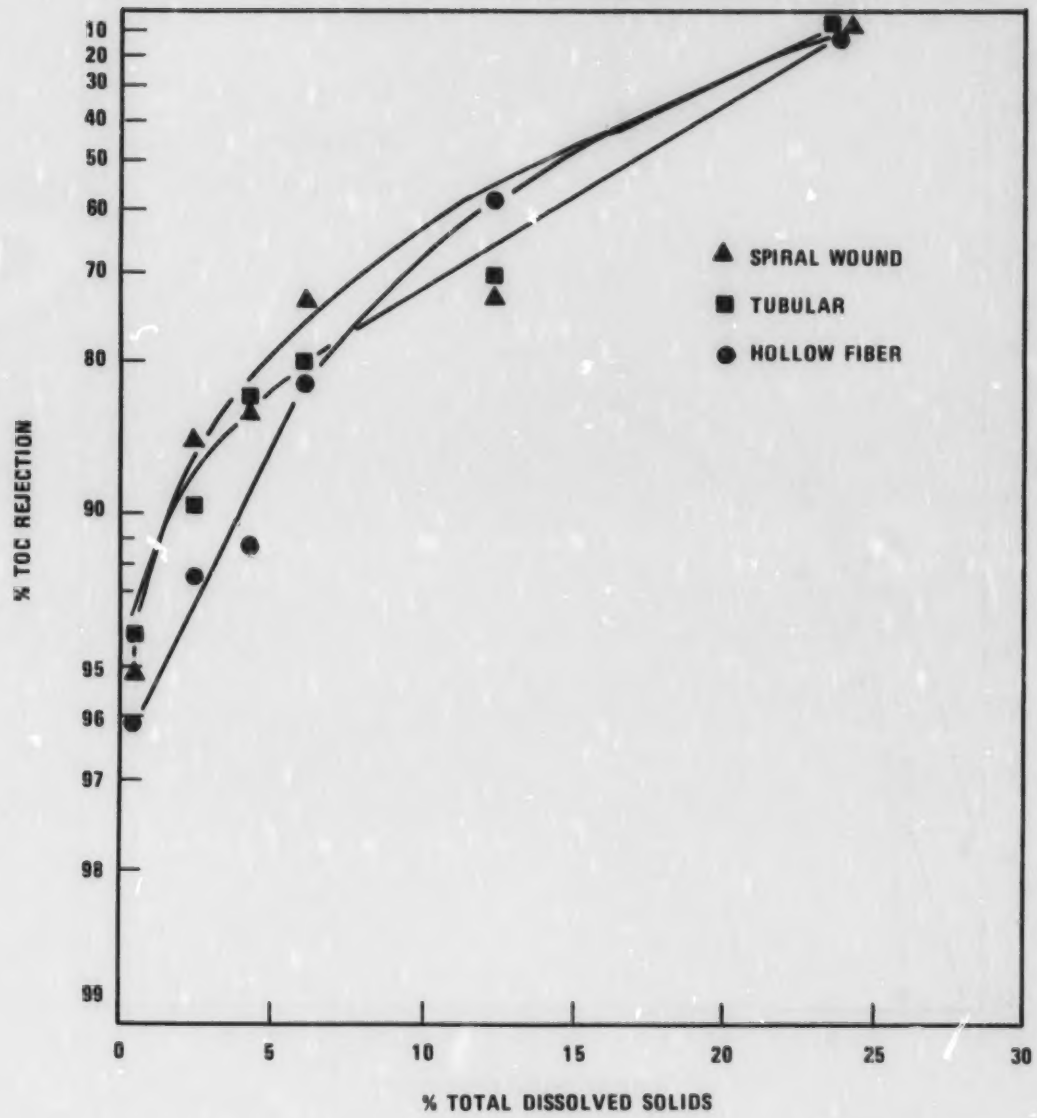

Figure 24. TOC* Rejection in Nickel Sulfamate Bath
* (Total Organic Carbon)

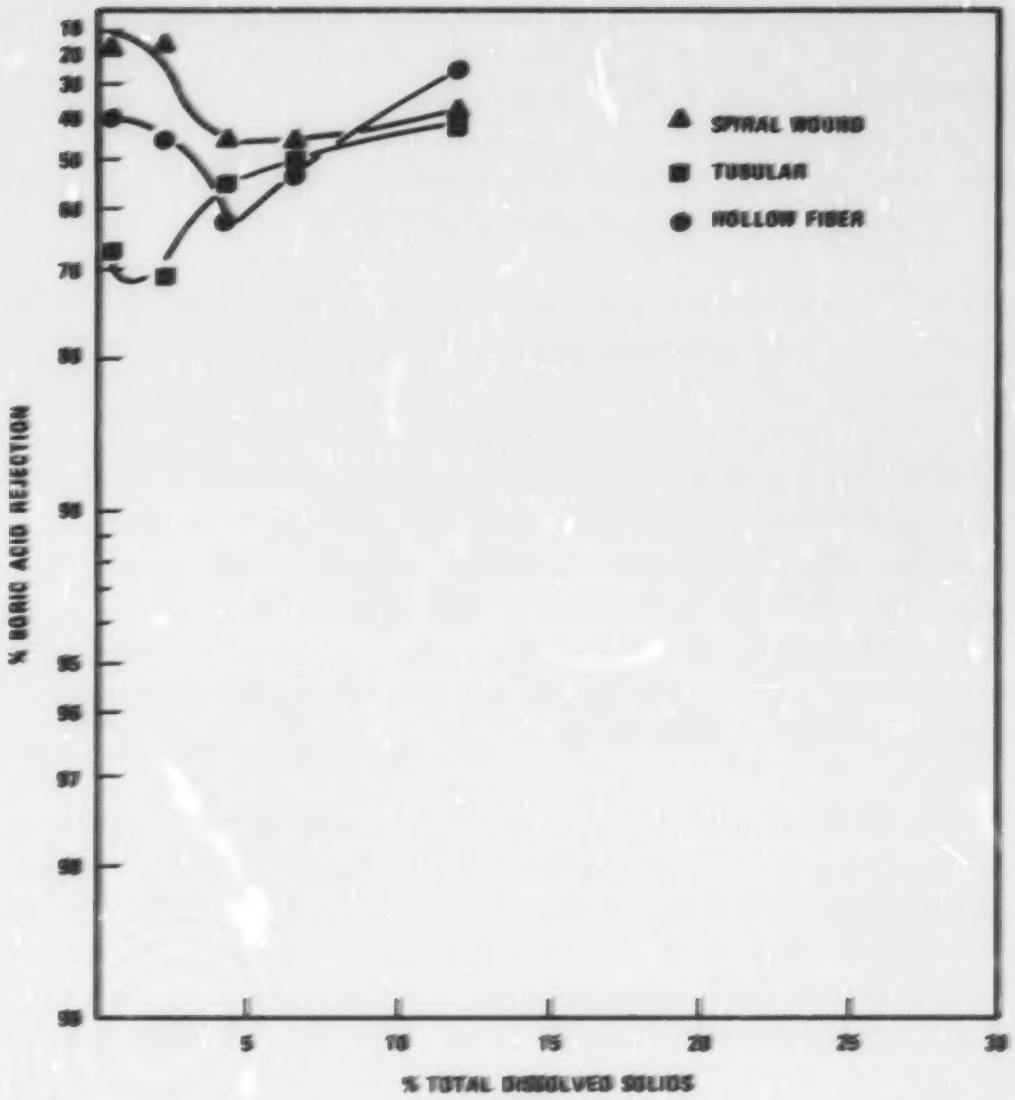

Figure 25. Boric Acid Rejection in Nickel Sulfamate Bath

degree of concentration by RO is not required. The poor rejection of boric acid is a potential limitation to RO treatment of this bath, but the loss of boric acid by selective permeation will not present a significant economic disadvantage when compared to the advantage of nickel recovery. However, the effect of its build-up in the rinse tanks should be given further consideration.

NICKEL FLUOBORATE

Tests were conducted on the nickel fluoborate bath using the tubular and hollow fiber modules. The data is summarized in Table 10.

Flux results are plotted in Figures 26 (hollow fiber module) and 27 (tubular module). The flux remained acceptable for both modules up to about 70% of bath concentration.

Rejection data are shown in Figures 28 (total solids) and 29 (nickel). Rejections for the hollow fiber module were significantly below those for the tubular module. This was because the hollow fiber module used in this test was the same module used in the life test with zinc cyanide, which was conducted prior to the nickel fluoborate tests. During the life test (discussed below) a decrease in rejection was observed and accounts for the poorer rejection performance of the hollow fiber module.

Based on the tubular module rejections, good nickel rejections were obtained up to about 70% of bath concentration (the highest concentration measured) and may well remain good to 100% of bath concentration. The total solids rejections were less favorable. Although boric acid rejections were not measured, selective boric acid permeation should be anticipated for this bath. Nevertheless, nickel fluoborate appears to be a very attractive candidate for RO treatment.

ZINC CHLORIDE

Flux and rejection data for the zinc chloride sample are given in Table 11. Flux and rejection for the zinc bath showed a rapid decline with increasing

Table 10. Experiment # 10 Nickel Fluoborate Bath

Feed Solutions		Membrane Module	Operating Conditions			Flux (gfd)	% Rejection	
% Solids[1]	% Bath[2]		Pressure (psi)	Temperature (°C)	pH of Feed		Total Dissolved Solids	Ni^{+2}
.88	3.4	Hollow Fiber	400	19	6.1	20.6	65	78
		Tubular	800	19	6.1	1.5	95	95
1.7	6.6	Hollow Fiber	400	20	4.9	19.2	67	74
		Tubular	800	20	4.9	1.2	93	95
2.5	10	Hollow Fiber	400	23	4.0	18.4	64	70
		Tubular	800	23	4.0	1.1	92	95
5.8	23	Hollow Fiber	400	23	3.4	10.9	60	74
		Tubular	800	23	3.4	.55	85	94
17	66	Hollow Fiber	400	25	3.0	5.6	44	72
		Tubular	800	25	3.0	.33	72	93

(1), (2) See Table 6

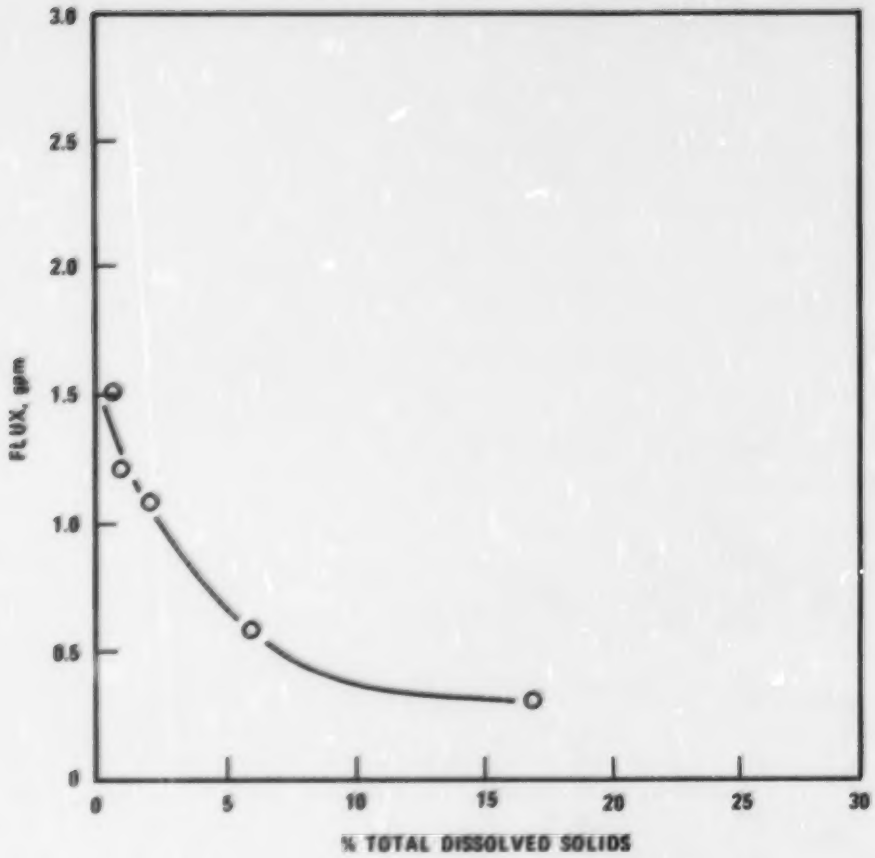

Figure 26. Flux in Nickel Fluoborate Bath
(Hollow Fiber Module)

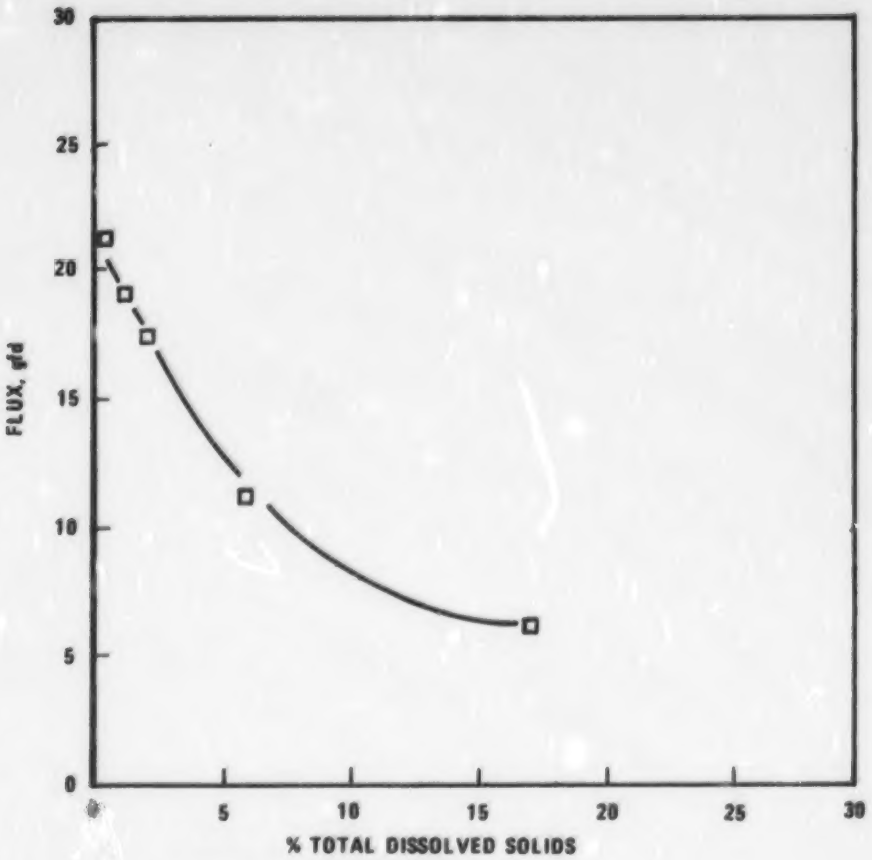

Figure 27. Flux in Nickel Fluoborate Bath
(Tubular Module)

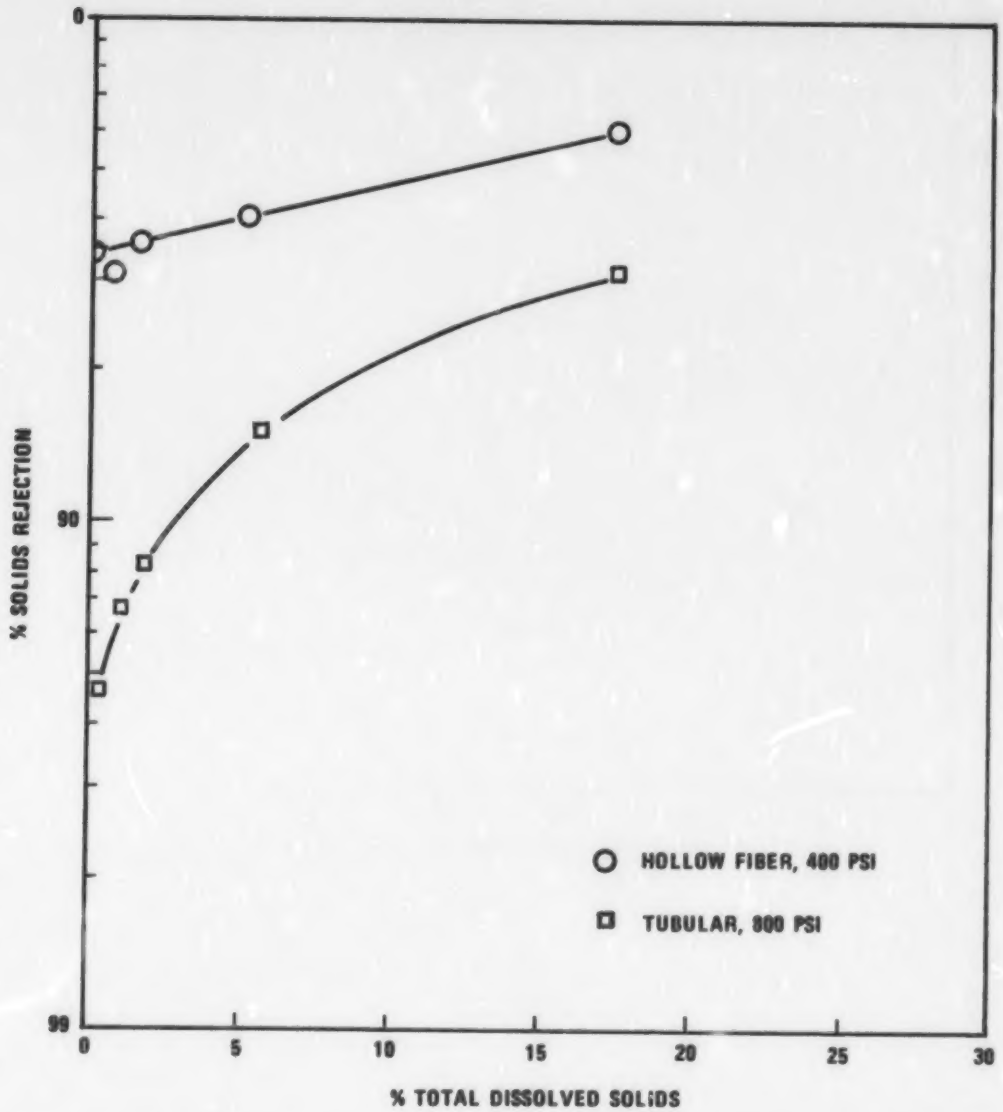

Figure 28. Solids Rejection in Nickel Fluoborate Bath

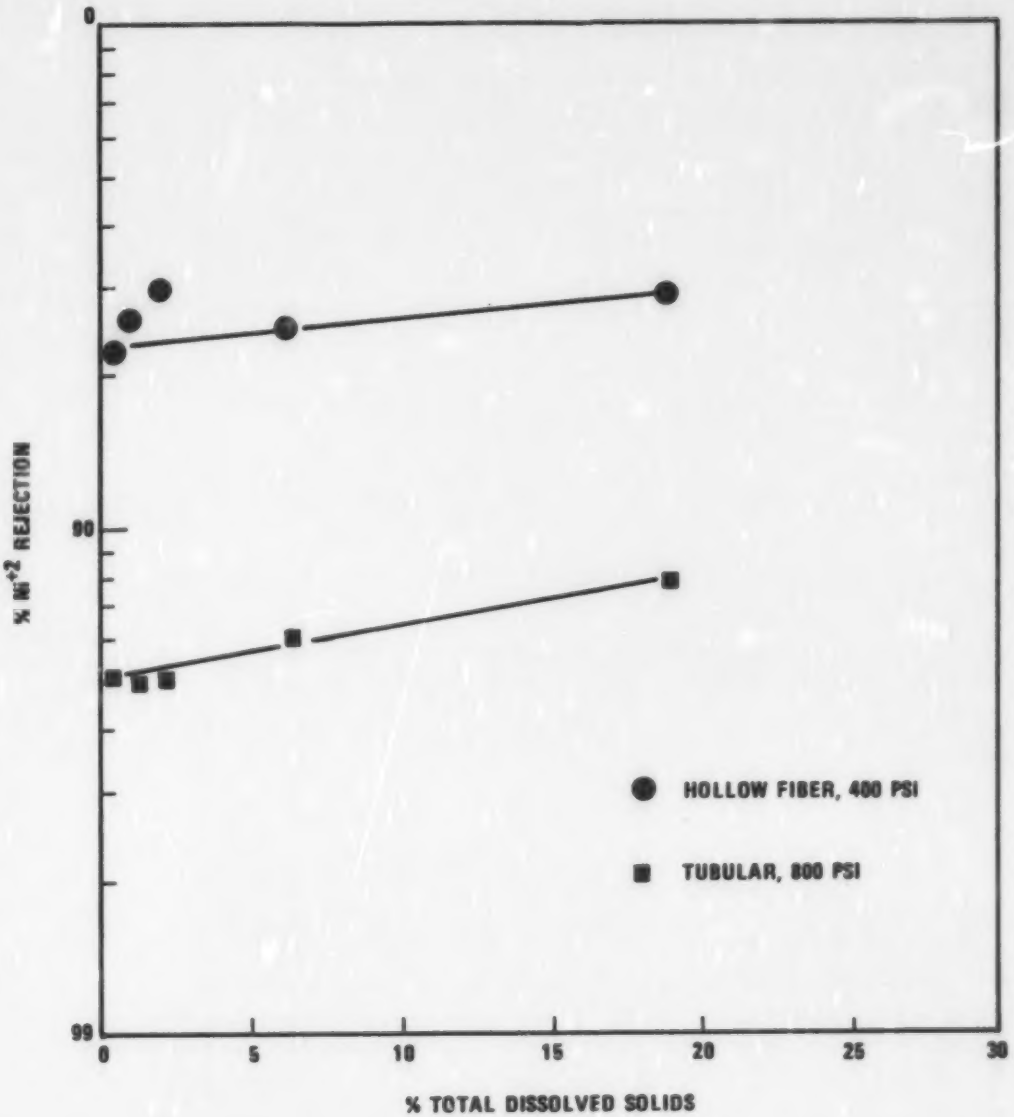

Figure 29. Ni^{+2} Rejection in Nickel Fluoborate Bath

Table 11. Experiment # 5 Zinc Chloride Bath

Feed Solutions		Membrane Module	Operating Conditions			Flux (gfd)	% Rejection	
% Solids[1]	% Bath[2]		Pressure (psi)	Temperature (°C)	pH of Feed		Total Dissolved Solids	Cl^-
.163	.82	Hollow Fiber	400	27	6.1	2.06	84.1	52.0
		Spiral	600			16.6	84.6	54.4
		Tubular	800			22.6	82.9	50.4
.644	3.25	Hollow Fiber	400	27	5.8	1.68	91.3	76.1
		Spiral	600			12.8	89.0	70.7
		Tubular	800			19.9	93.4	80.9
1.58	8.0	Hollow Fiber	400	28	5.5	.96	93.7	84.3
		Spiral	600			9.33	92.2	81.7
		Tubular	800			15.1	92.7	82.6
4.19	21.2	Hollow Fiber	400	29	5.3	.11	95.6	90.0
		Spiral	600			5.07	93.7	86.8
		Tubular	800			9.62	88.5	78.3
4.86	24.5	Hollow Fiber	400	30	5.0	.03	73.9	65.9
		Spiral	600			2.54	77.6	69.0
		Tubular	800			5.23	88.6	83.4
11.82	60.0	Hollow Fiber	400	30	4.7	.014	30.0	17.1
		Spiral	600			.58	42.7	31.7
		Tubular	800			.230	53.9	41.5

(1), (2) See Table 6

feed concentration. Since zinc chloride complexes are of relatively low-molecular weight, this demonstrates that molarity is the important concentration parameter in controlling flux and rejection. The fluxes for the tubular and spiral wound modules (Figure 30) were high at low concentrations, but fell rapidly to good and acceptable values at 20% of bath concentration (5% TDS). Flux was acceptable for the hollow fiber module (Figure 31) up to only one-half this concentration.

Rejections showed a pronounced maximum for all three modules based on both TDS concentration (Figure 32) and Cl^- concentration (Figure 33). The three modules behaved very similarly with no improvement under increasing operating pressure, except at the unacceptably low rejections at higher concentrations. The increased rejection with increasing concentration is attributed to the following phenomenon. At low concentration, the zinc chloride complex is highly dissociated, and a major proportion of the zinc and chloride exists as free ions. At intermediate concentrations, a much greater proportion is complexed as a higher molecular weight species, more readily rejected by the membrane. Rejections were good up to about 20% of bath concentration (5% TDS) based on TDS concentration, but were only acceptable to fair up to this feed strength based on Cl^- concentration.

Based on these results, zinc chloride does not appear to be as attractive a candidate as copper pyrophosphate, nickel sulfamate, and nickel fluoborate. Rinse water cannot be concentrated to as great a degree and there is no substantial evaporative loss from the zinc chloride bath (which operates at ambient temperature). Therefore, substantial auxiliary evaporation would be required for closed-loop treatment.

CADMIUM CYANIDE

The high pH range of all cyanide baths excludes the use of cellulose acetate membranes. Consequently, only the hollow-fiber polyamide membrane module was employed in these experiments.

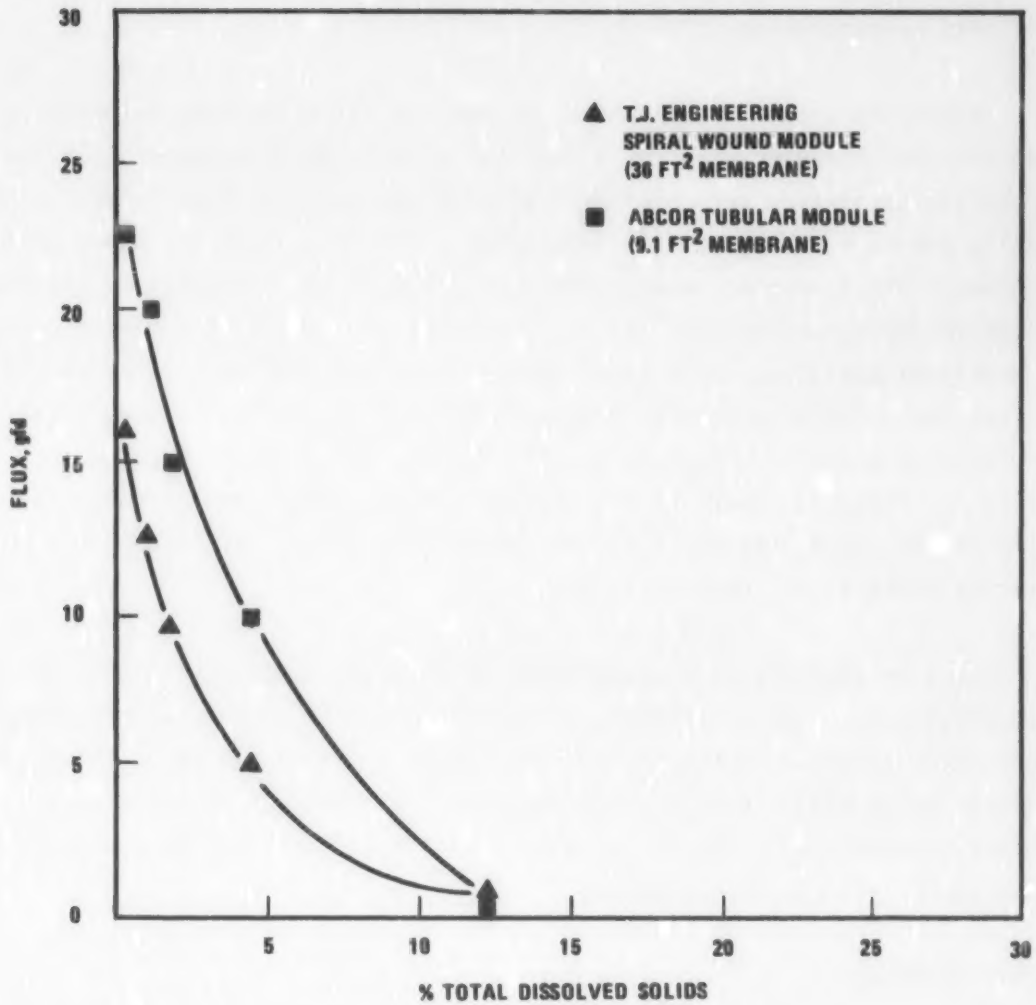

Figure 30. Flux in Zinc Chloride Bath

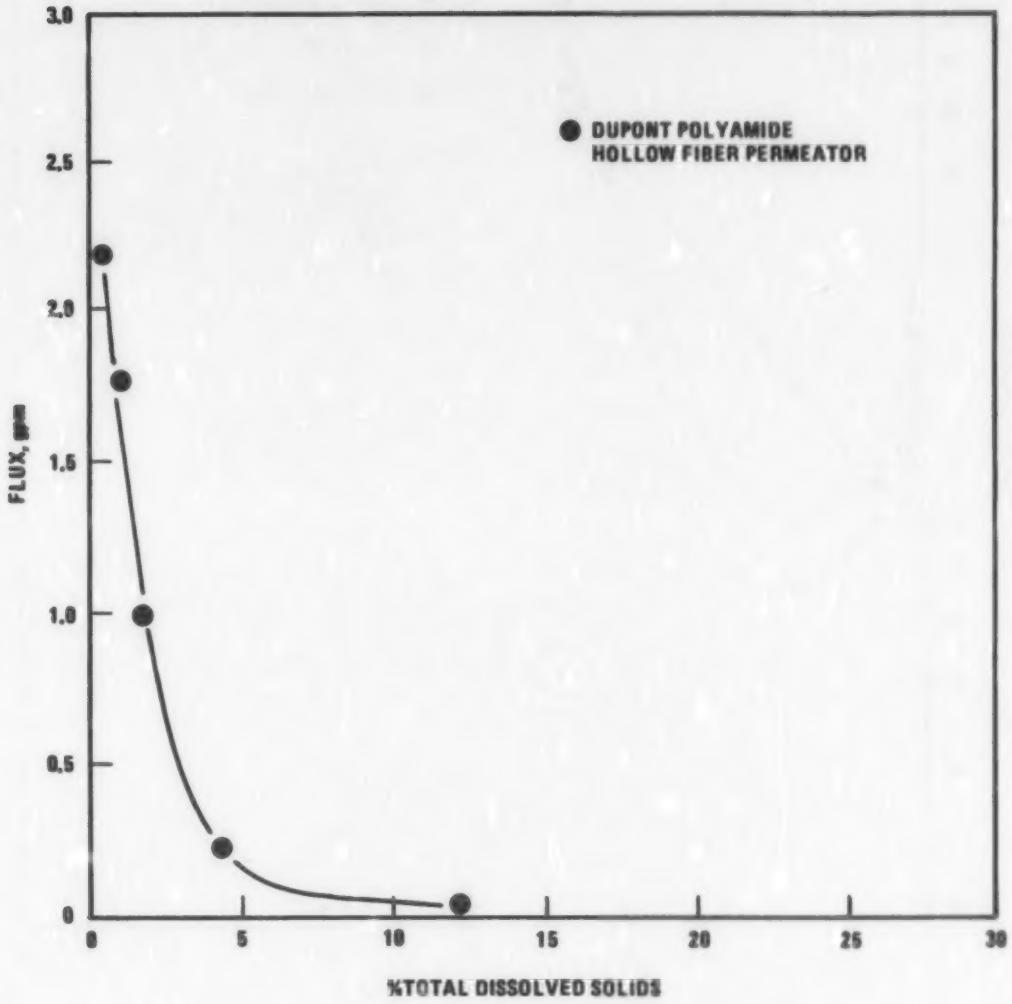

Figure 31. Flux in Zinc Chloride Bath

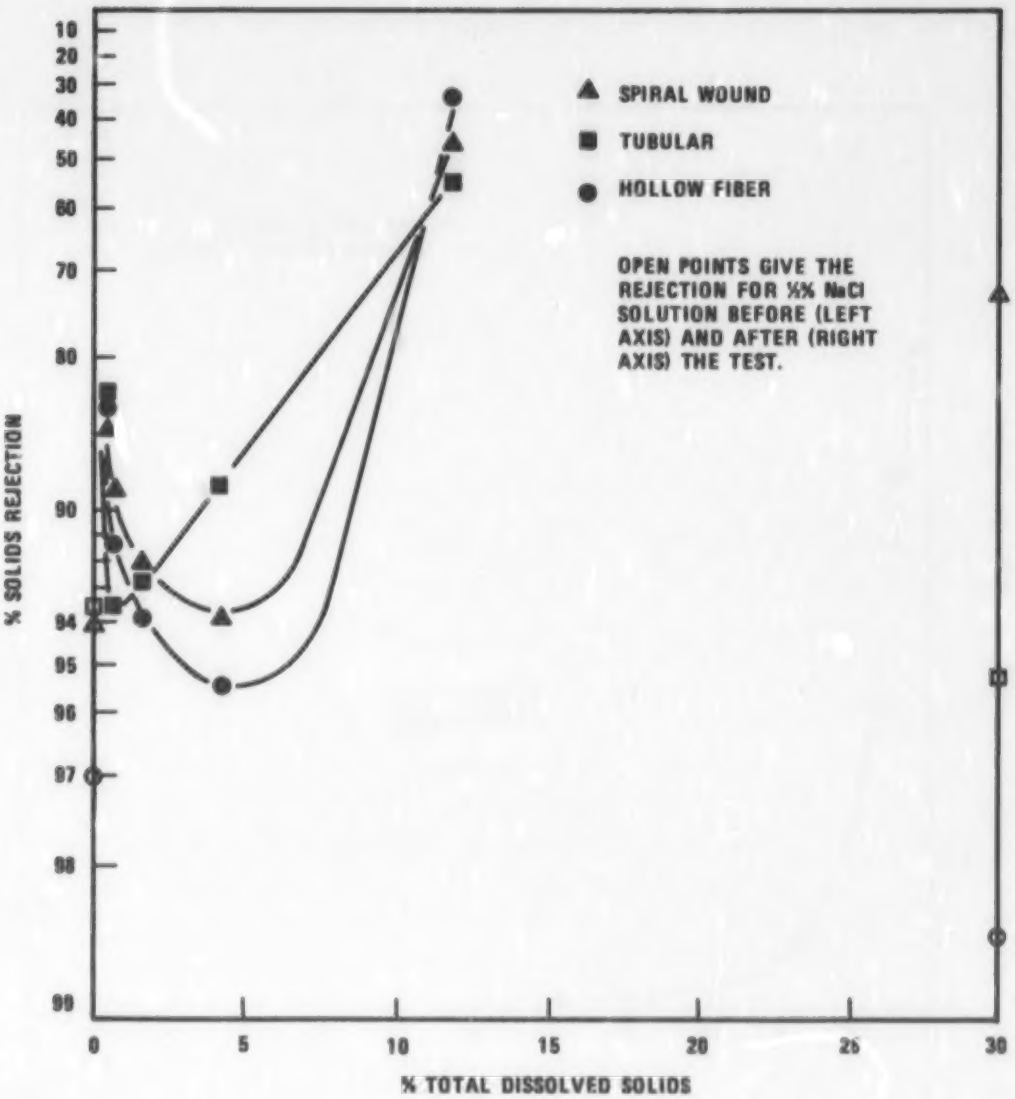

Figure 32. Solids Rejection in Zinc Chloride Bath

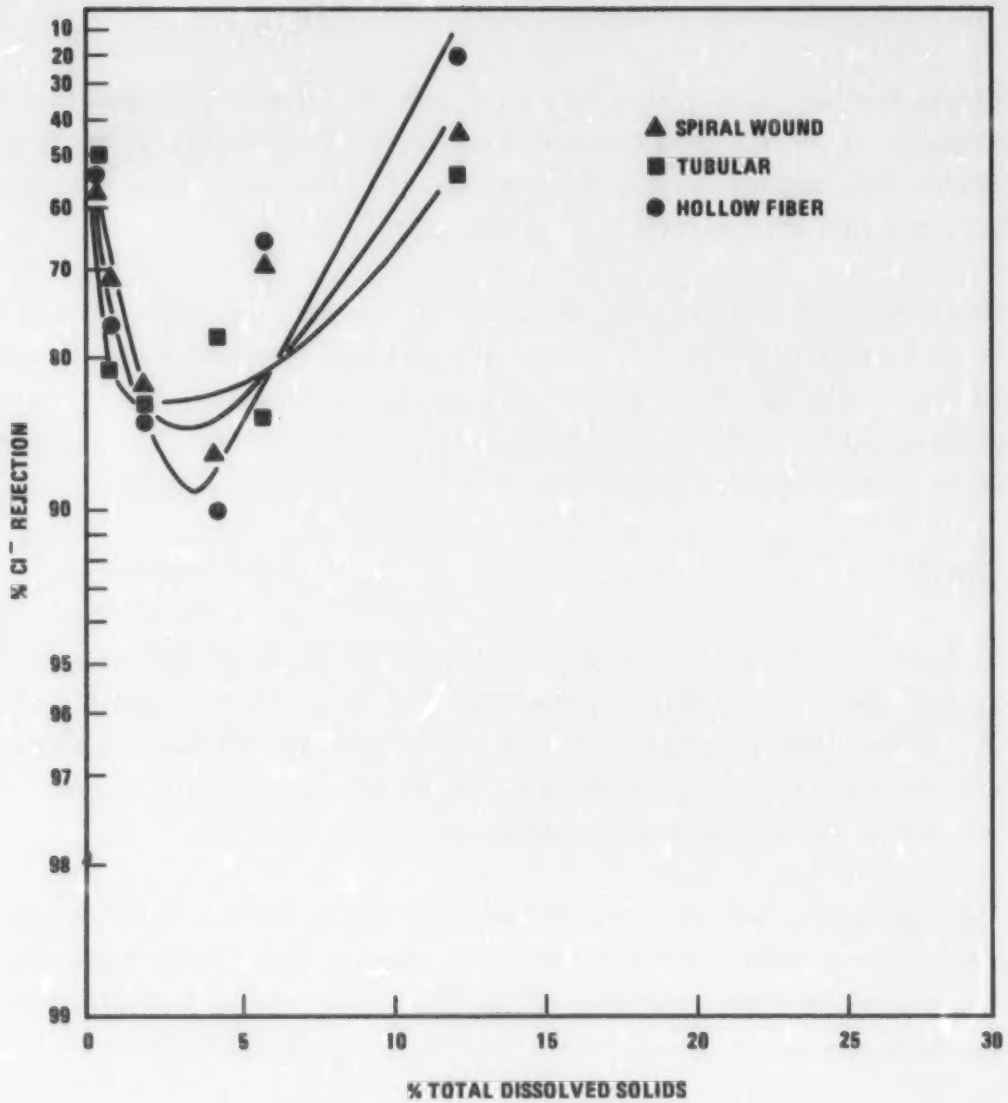

Figure 33. Cl^- Rejection in Zinc Chloride Bath

The cadmium cyanide bath tested had a solids content intermediate between that of the zinc cyanide, on the low side, and the copper cyanide bath, on the high side. The flux and rejection results were intermediate, accordingly, in line with the theory discussed above. A summary of the data is shown in Table 12.

Fluxes for this system are given in Figure 34 and were acceptable up to approximately 10% of the bath concentration (3.5% TDS). Rejection based on TDS (Figure 35), cadmium (Figure 36), and cyanide (Figure 37) were good up to nearly double this concentration.

While these results indicate that cadmium cyanide rinse waters can be treated with reverse osmosis, it is evident that the full bath strength cannot be obtained. Since cadmium cyanide baths operate at close to ambient temperature where evaporative losses are small, it is likely that auxiliary evaporation would be required for closed-loop treatment of cadmium cyanide.

ZINC CYANIDE

On the basis of solids content, the results of flux and rejection for the zinc system (Table 13) were nearly identical for those of the cadmium system. However, because the solids content of the zinc plating bath was low compared to the cadmium and copper systems, concentrates of a higher fraction of bath strength can be successfully generated by RO.

The flux data shown in Figure 38 indicate that performance was acceptable up to 25 to 30% of bath concentration (approximately 3.2% TDS). Rejection data given in Figures 39 (total solids), 40 (Zn^{+2}), and 41 (CN^{-}), indicate that rejections were good up to 20% of bath strength, and acceptable up to 30%.

Based on these results, zinc cyanide appears to be an attractive candidate for RO treatment. However, as in the case of cadmium cyanide, zinc cyanide is an ambient-temperature bath, and auxiliary evaporation would probably be required for closed-loop treatment.

Table 12. Experiment # 6 Cadmium Cyanide Bath

Feed Solutions		Membrane Module	Operating Conditions			Flux (gpm)	% Rejection		
% Solids[1]	% Bath[2]		Pressure (psig)	Temperature (°C)	pH of Feed		Total Dissolved Solids	Cd^{++}	CN^-
.31	1	Hollow Fiber	400	28	11.5	2.1	98	99+	83
1.03	4	Hollow Fiber	400	28	11.8	1.6	89	99+	97
2.43	9	Hollow Fiber	400	27	12.2	.67	97	99+	95
3.12	12	Hollow Fiber	400	27	12.5	.24	96	99	92
9.82	37	Hollow Fiber	400	27	12.9	.028	9.2	78	10

(1), (2) See Table 6

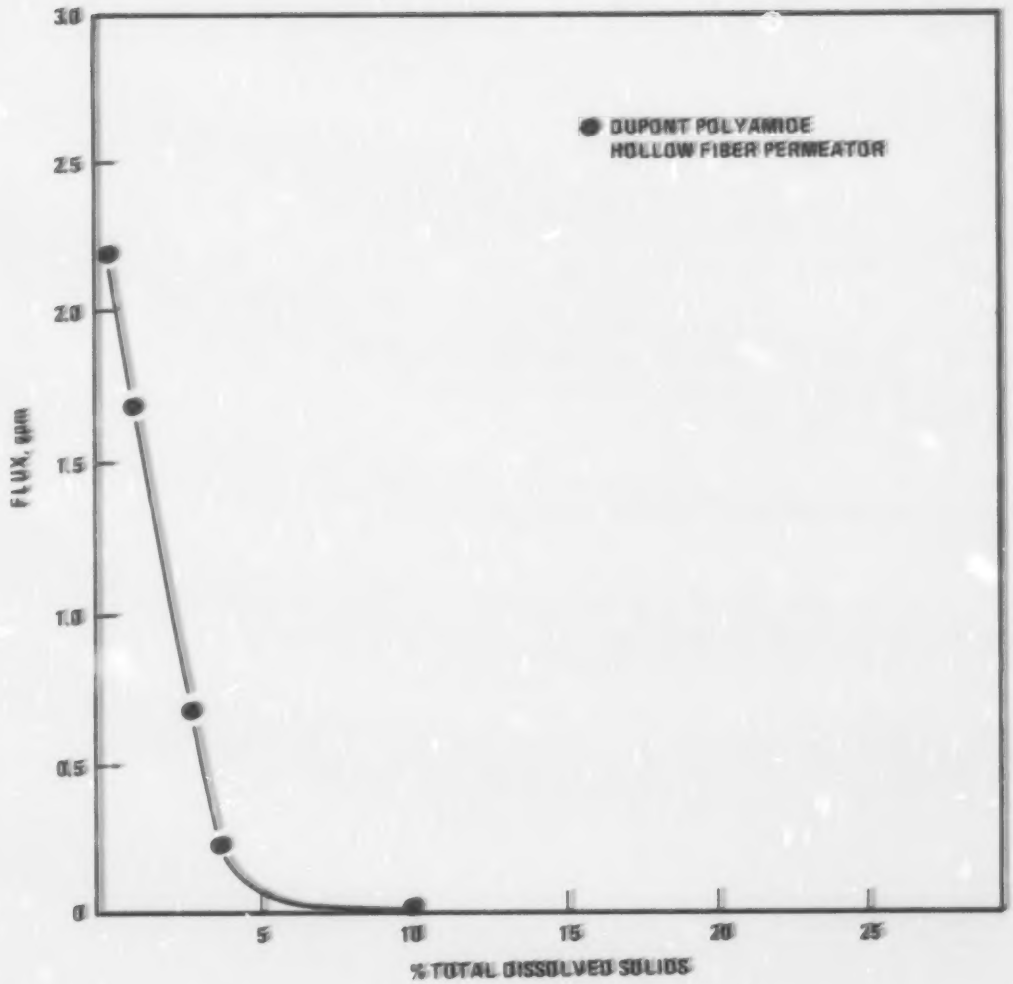

Figure 34. Flux in Cadmium Cyanide Bath

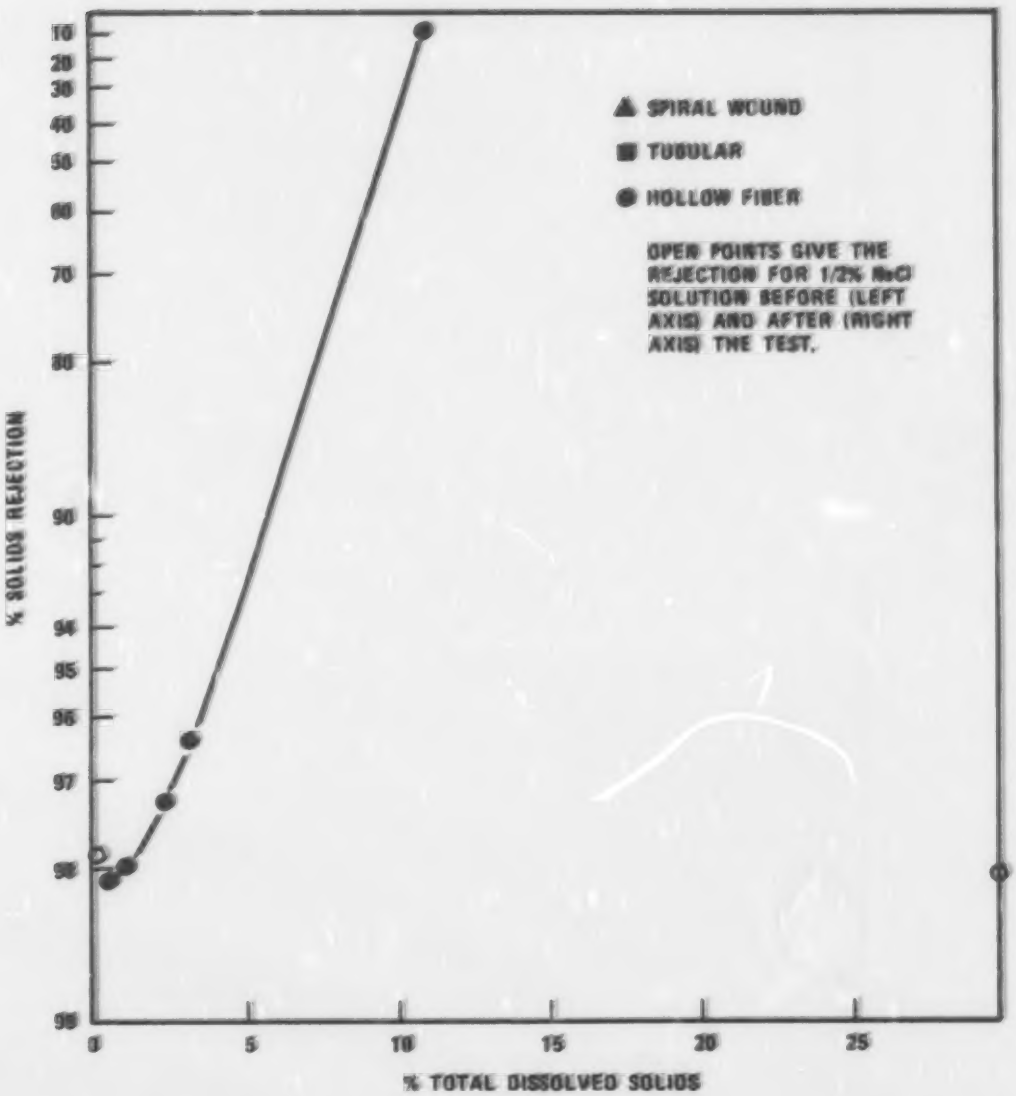

Figure 35. Solids Rejection in Cadmium Cyanide Bath

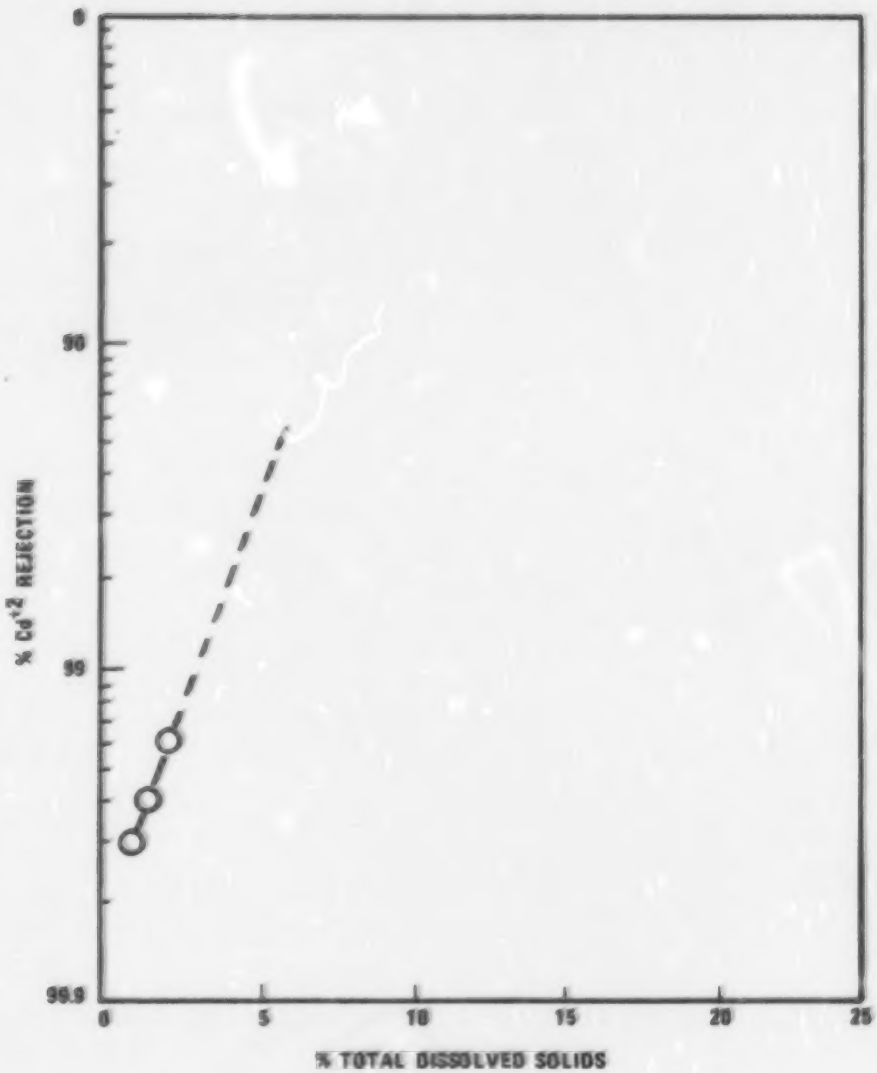

Figure 36. Cd^{+2} Rejection in $Cd(CN)_2$ Bath

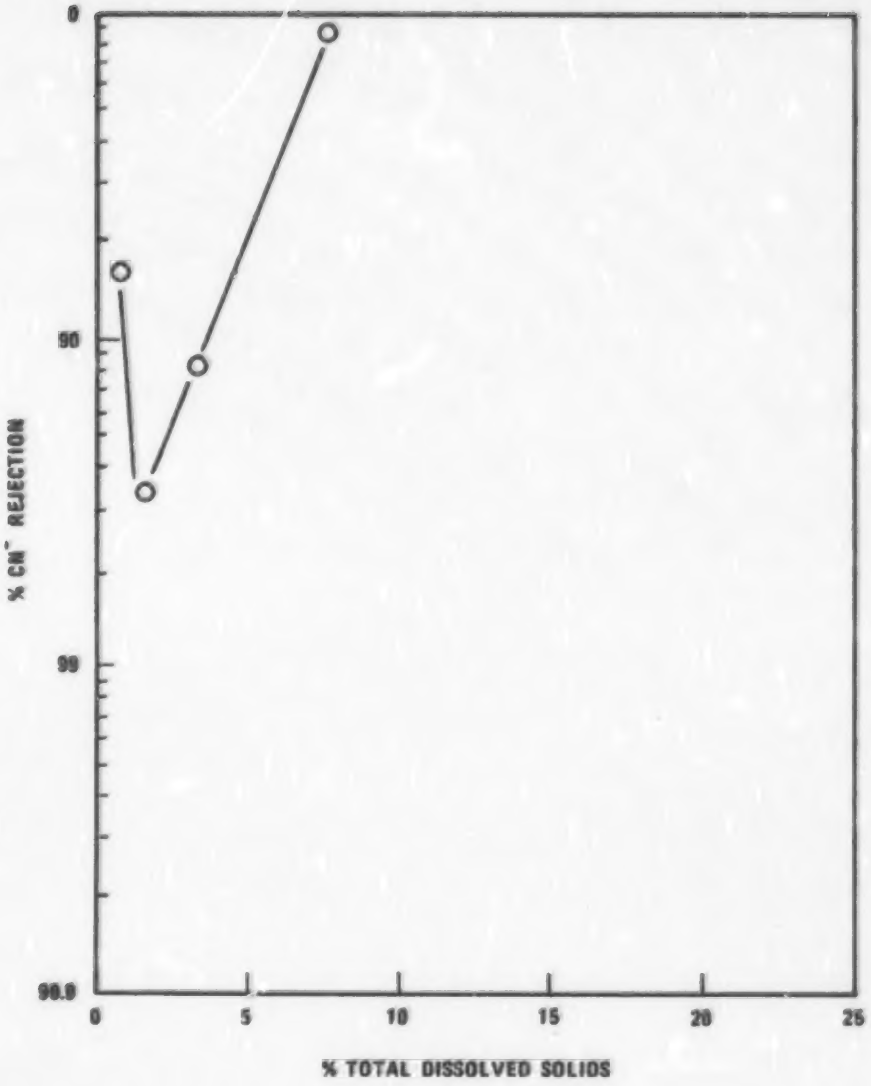

Figure 37. CN^- Rejection in $Cd(CN)_2$ Bath

Table 13. Experiment # 7 Zinc Cyanide Bath

Feed Solutions		Membrane Module	Operating Conditions			Flux (gpm)	% Rejection		
% Solids[1]	% Bath[2]		Pressure (psig)	Temperature (°C)	pH of Feed		Total Dissolved Solids	Zn	CN^-
.47	4	Hollow Fiber	400	27	12.3	1.8	97	98	85
.77	7	Hollow Fiber	400	27	12.6	1.6	97	99+	99+
1.27	11	Hollow Fiber	400	27	12.8	1.2	96	99+	99
2.44	21	Hollow Fiber	400	27	13.3	.58	90	99+	97
4.05	36	Hollow Fiber	400	27	13.7	.21	70	98	97

(1), (2) See Table 6

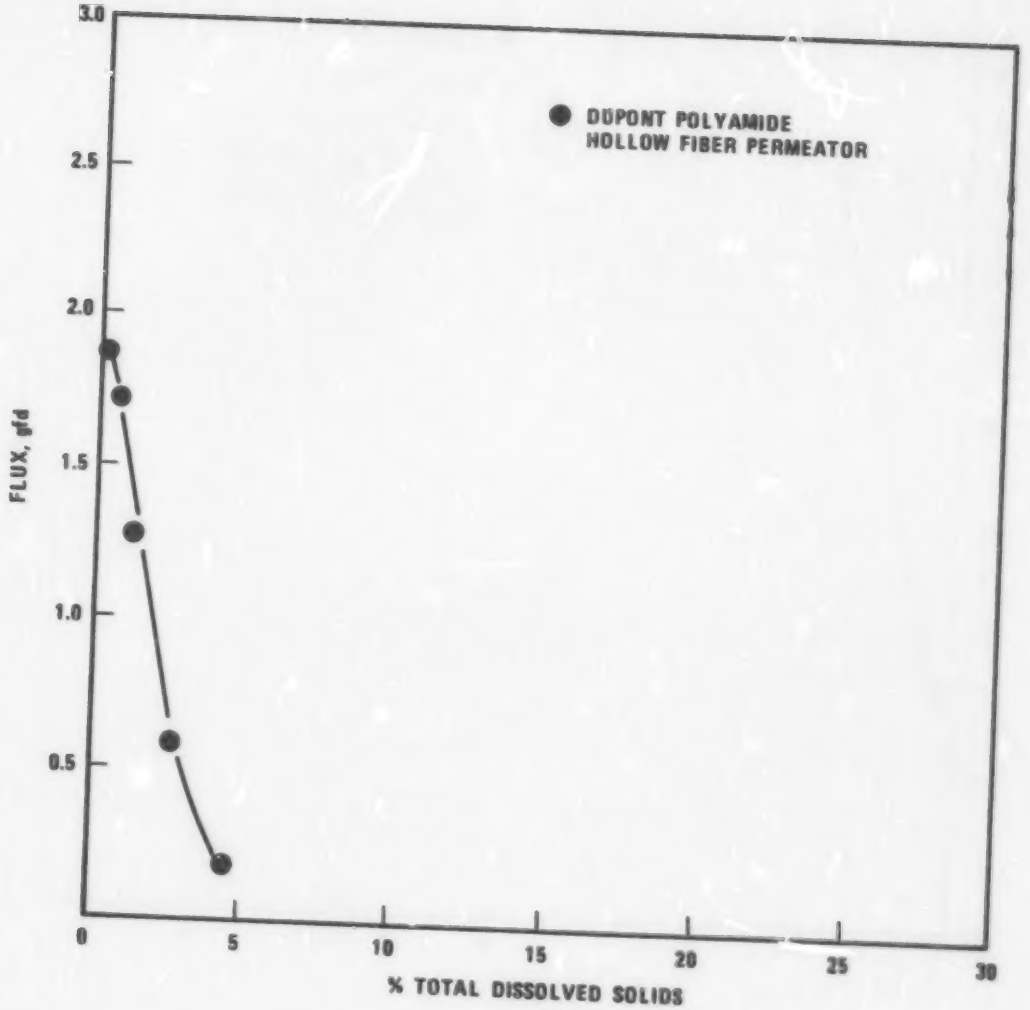

Figure 38. Flux in Zinc Cyanide Bath

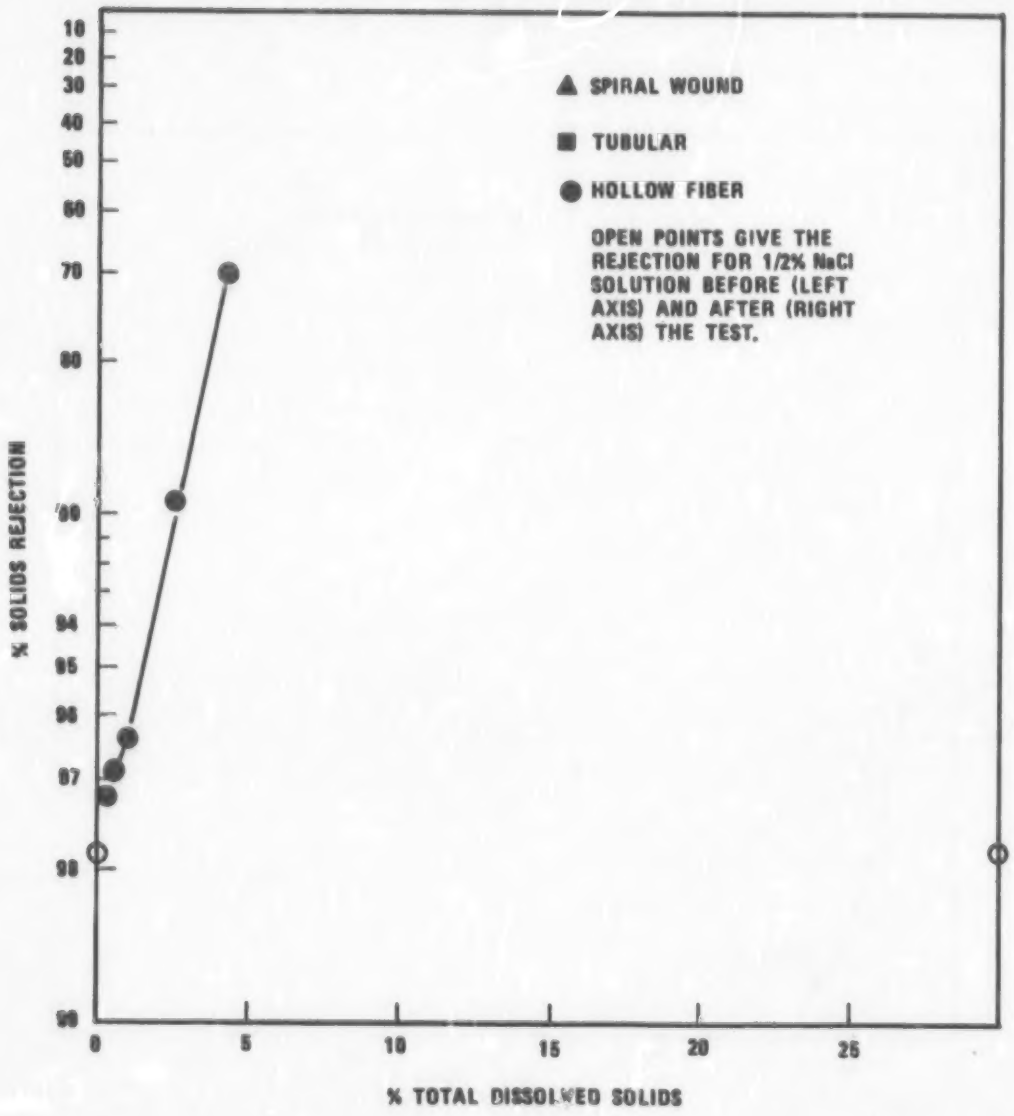

Figure 39. Solids Rejection in Zinc Cyanide Bath

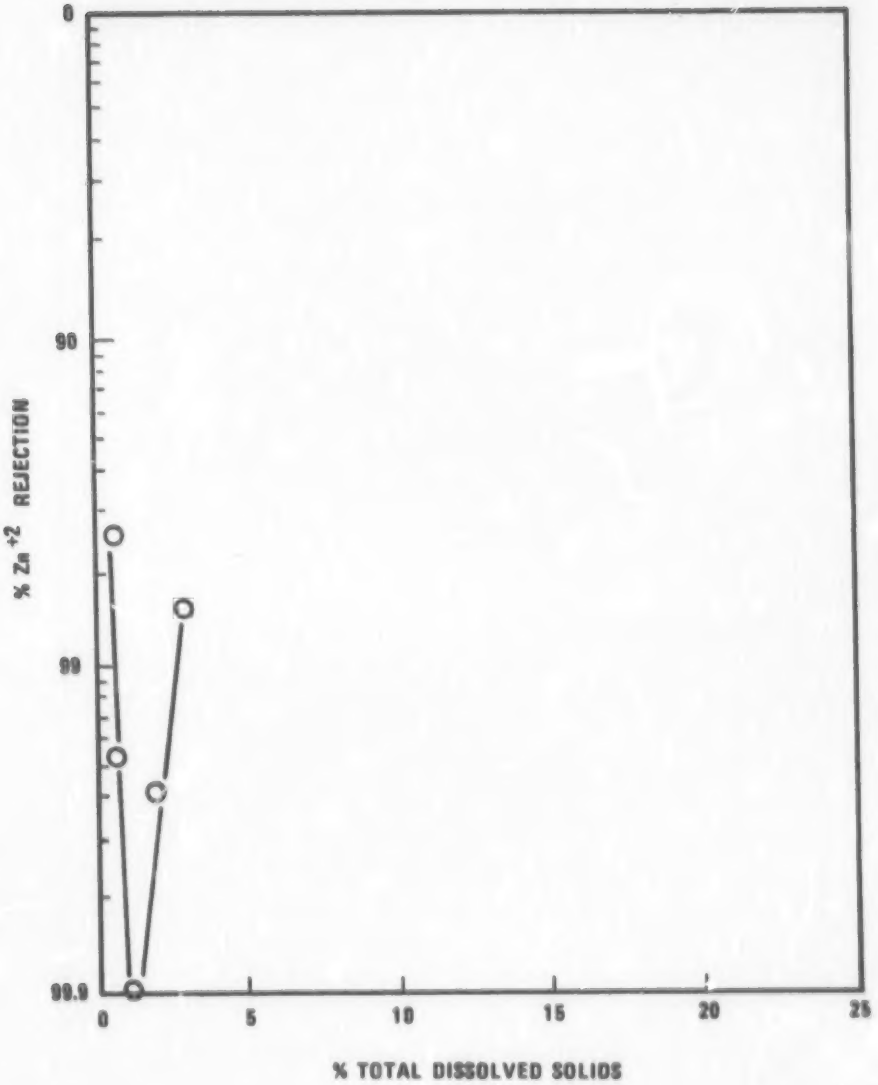

Figure 40. Zn^{+2} Rejection in $Zn(CN)_2$ Bath

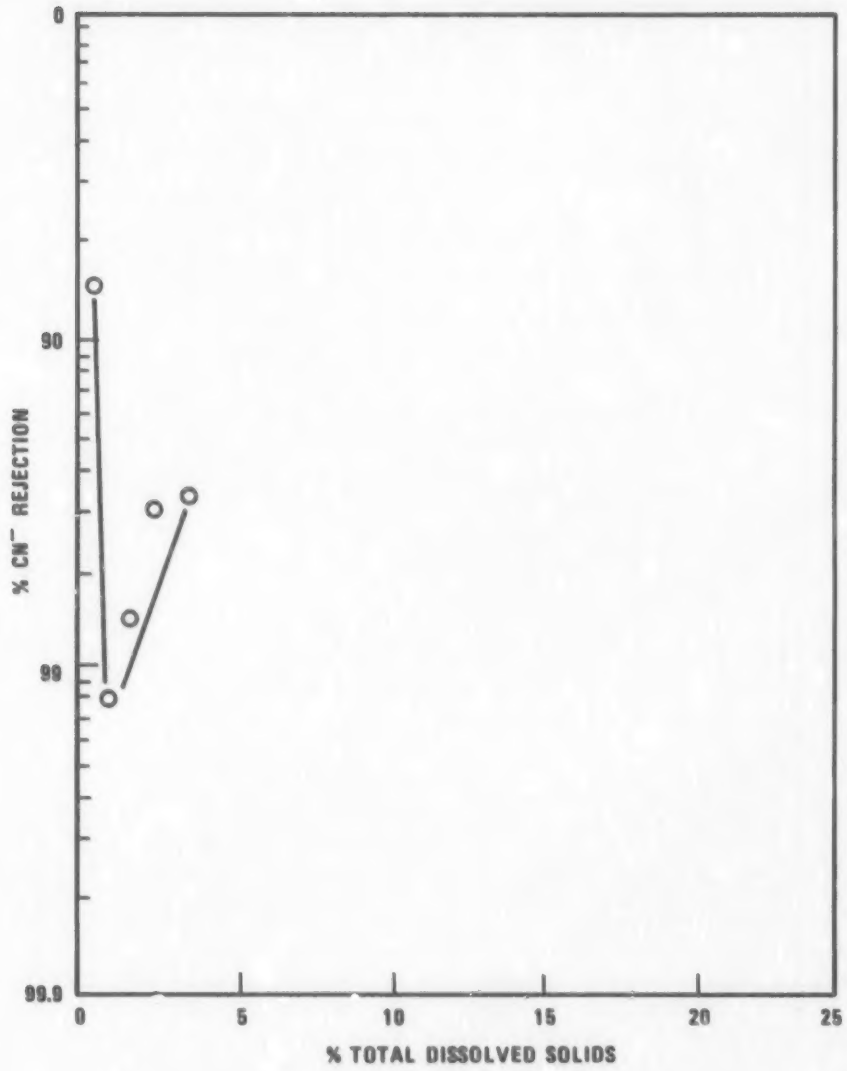

Figure 41. CN^- Rejection in $Zn(CN)_2$ Bath

COPPER CYANIDE

The copper cyanide plating bath, having a solids content 65% higher than the cadmium cyanide bath and 4.5 times that of the zinc cyanide bath, showed markedly poorer flux and rejection behavior as a function of fraction of plating bath strength (see Table 14).

As shown in Figure 42, fluxes for the copper cyanide rinse waters were acceptable up to a feed concentration of only 7 to 8% of bath strength (approximately 4% TDS). Rejections, shown in Figures 43 (total solids), 44 (Cu^{++}), and 45 (CN^{-}), were seen to be good up to only 10% of bath strength (5.5% TDS).

Although these results indicate that a high degree of concentration cannot be obtained with RO, copper cyanide is still an attractive application. Copper cyanide baths are operated at temperatures between 60 and 82°C (140 and 180°F), and evaporative losses are significant. Therefore, it is still possible to close the loop with RO even though a highly concentrated stream is not produced.

ROCHELLE COPPER CYANIDE

Test results for a Rochelle copper cyanide bath are shown in Table 15. The flux, plotted in Figure 46, remained acceptably high even at 26% of bath concentration (3.3% TDS).

Rejections, plotted in Figure 47, were exceptionally good, particularly at the higher feed concentrations. At 26% of bath concentration rejections of total solids, conductivity, copper, and cyanide were all above 90%. In addition, this bath operates at elevated temperatures so that a high degree of concentration is not required. Thus, the standard Rochelle copper cyanide bath appears to be a very attractive application for closed-loop RO treatment.

RESULTS FOR CYANIDE LIFE TEST

Membrane processing of electroplating rinse waters will be of interest only if an economically viable membrane life can be obtained. What is

Table 14. Experiment # 8 Copper Cyanide Bath

Feed Solutions		Membrane Module	Operating Conditions			Flux (gpm)	% Rejection		
% Solids[1]	% Bath[2]		Pressure (psig)	Temperature (°C)	pH of Feed		Total Dissolved Solids	Cu^{++}	CN^{-}
.57	2	Hollow Fiber	400	26	11.8	1.8	98	99+	92
1.93	5	Hollow Fiber	400	26	12.2	1.2	98	99+	99+
3.71	10	Hollow Fiber	400	26	12.5	.62	97	99+	99+
7.98	22	Hollow Fiber	400	27	12.9	.076	77	84	92

(1), (2) See Table 6

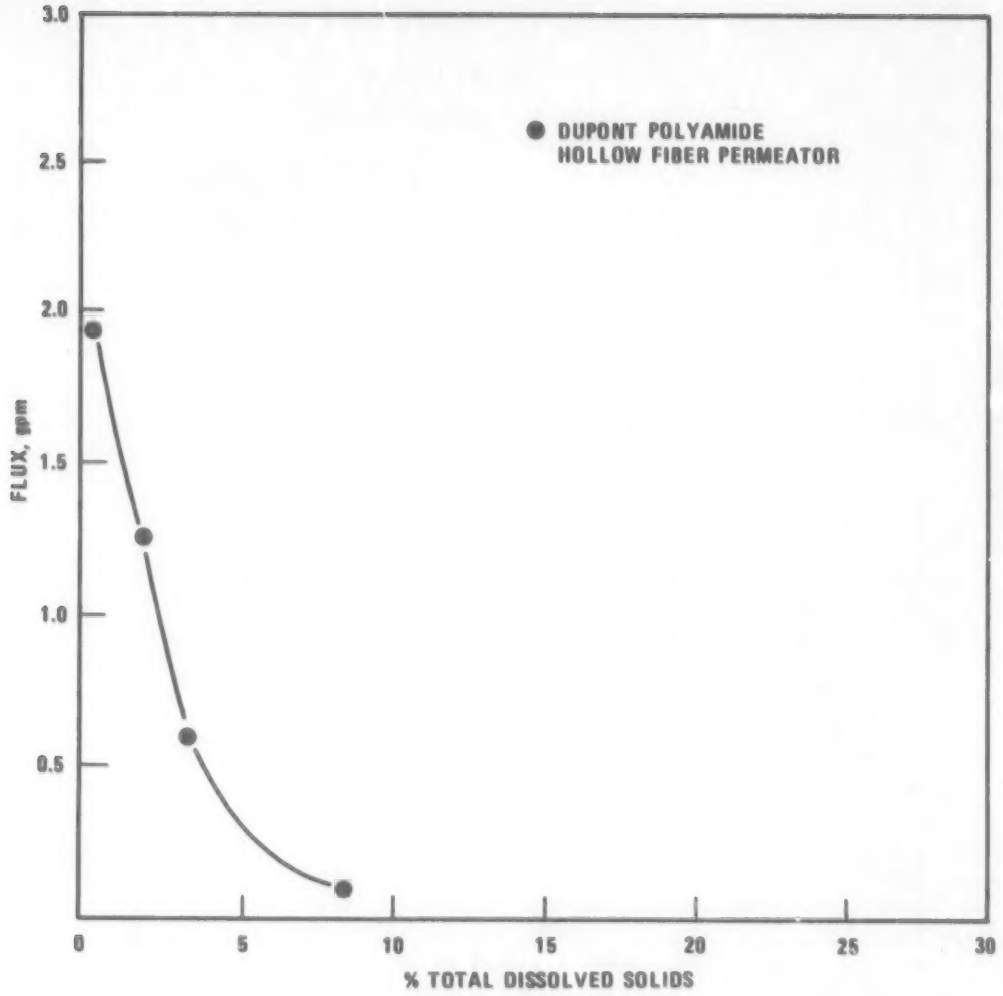

Figure 42. Flux in Copper Cyanide Bath

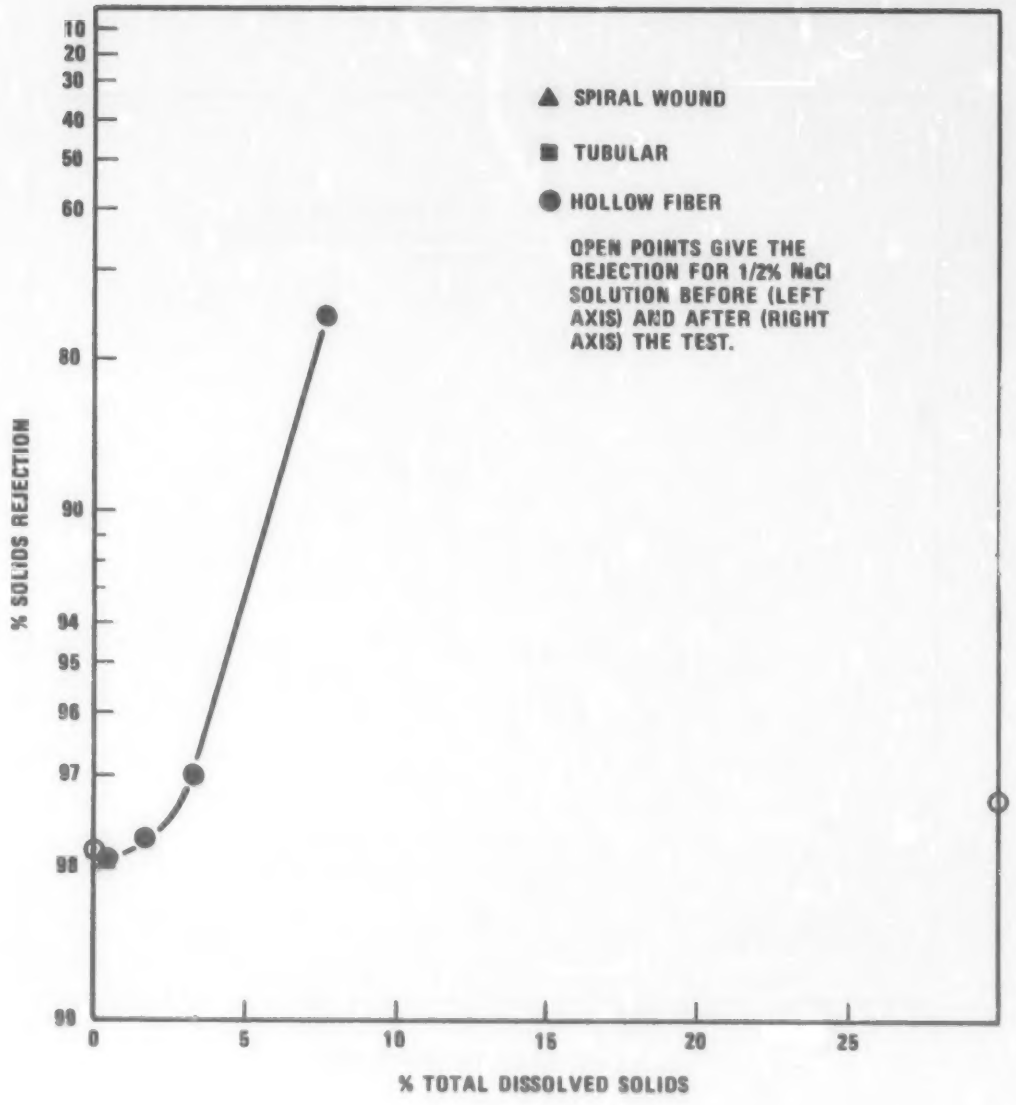

Figure 43. Solids Rejection in Copper Cyanide Bath

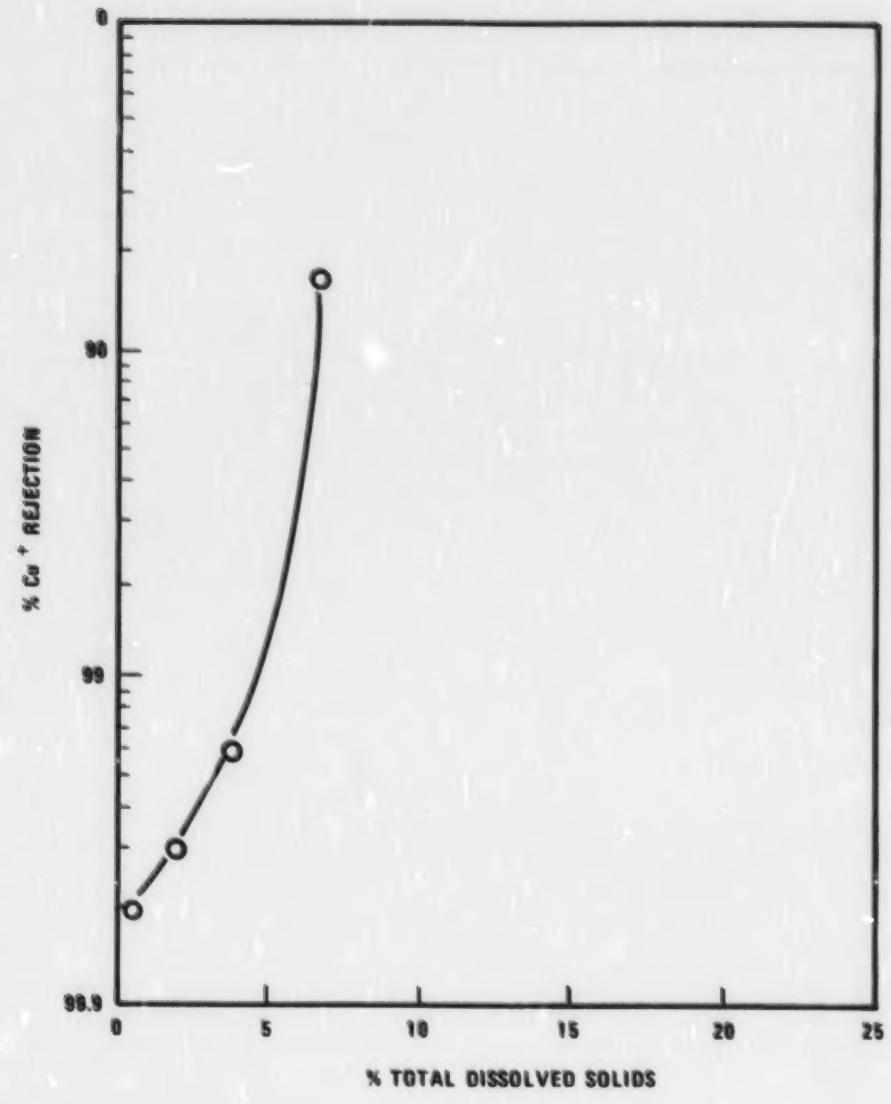

Figure 44. Cu^{+} Rejection in CuCN Bath

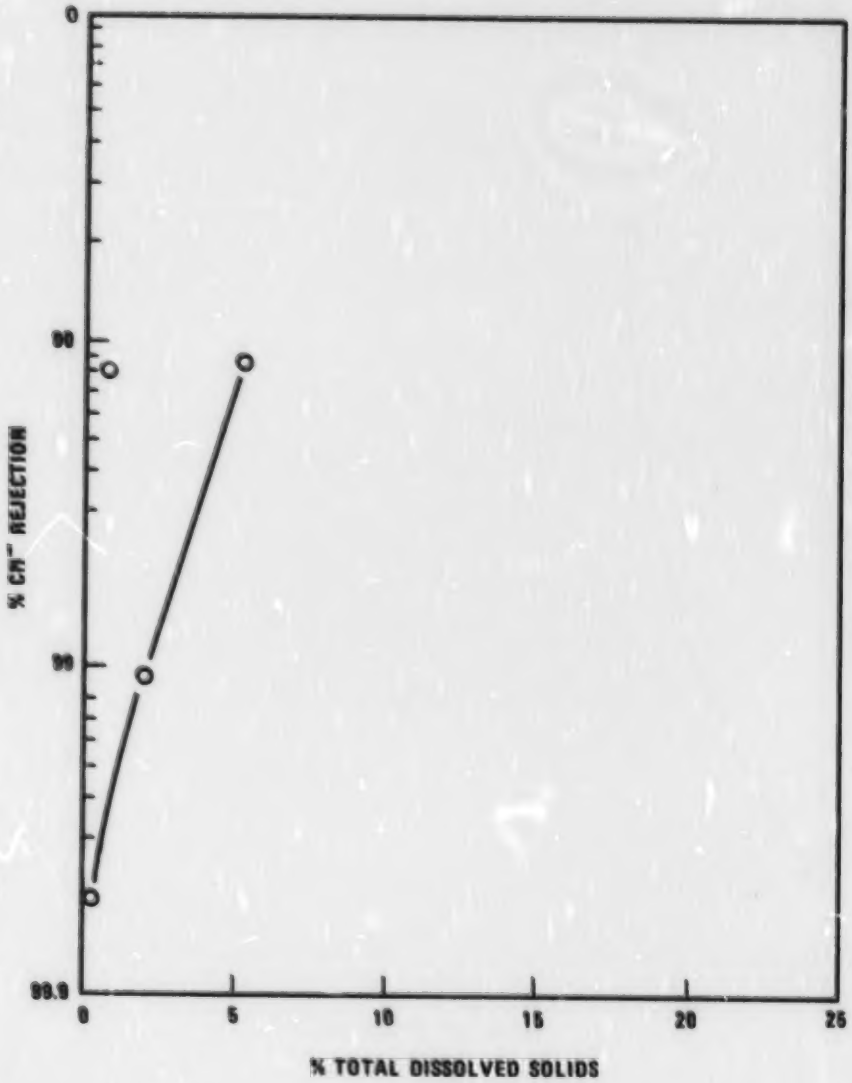

Figure 45. CN^- Rejection in CuCN Bath

Table 15. Experiment # 11 Rochelle Copper Cyanide Bath

Feed Solutions		Membrane Module	Operating Conditions			Flux (gpm)	% Rejection			
% Solids	% Bath		Pressure (psig)	Temperature (°C)	pH of Feed		Total Dissolved Solids	Conductivity	Cu^{+}	CN^{-}
3.34	26.3	Hollow Fiber	400	25	10.6	1.60	98.5	93	96.6	94.9
1.35	10.6	Hollow Fiber	400	28	10.1	2.06	98.1	92	97.3	94.7
.132	1.04	Hollow Fiber	400	28	9.8	2.54	96.0	82	89.6	64.7

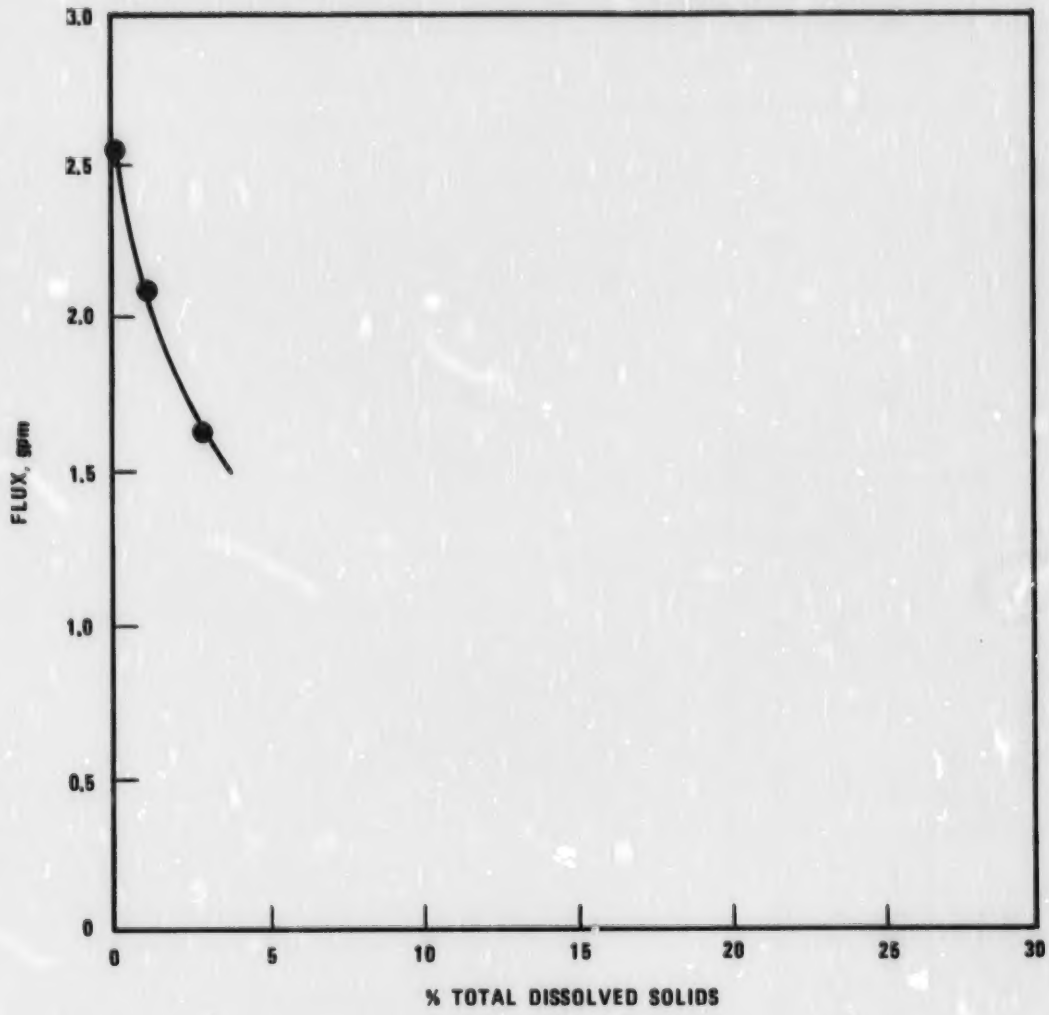

Figure 46. Flux in Rochelle Copper Cyanide Bath

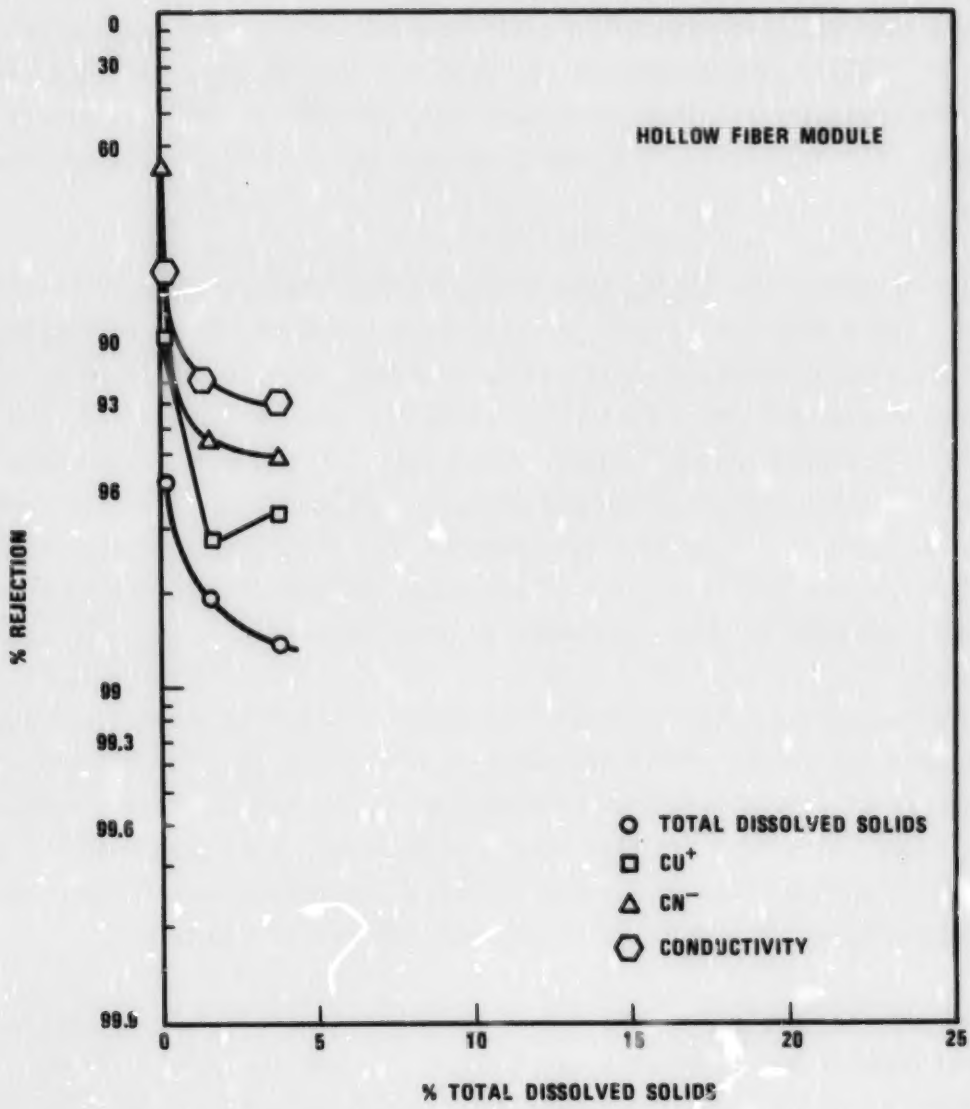

Figure 47. Rejection in Rochelle Copper Cyanide Bath

economically attractive depends, of course, on overall process economics. As a guide, however, a membrane life of six months or more would seem desirable.

In order to study long-term irreversible changes in membrane performance, an extended test was performed using a zinc cyanide bath at one-tenth bath concentration. Usually, the system was operated for nine hrs/day, five days/week. However, the permeator remained in contact with the plating solution at all other times. For most of the life tests, pH was adjusted to 11.5 by addition of H_2SO_4.

Figure 48 summarizes the history of the hollow-fiber module used in the life test. The module was exposed to various plating bath solutions ranging in pH from 3.3 to 13.9, and ranging in solute concentrations from 0.3% up to 24%, for a total of over 800 hrs. During approximately half of this period, the system was in operation at 29.1 kg/cm^2 (400 psig). Flux and rejection data for a 0.5% NaCl solution were obtained periodically throughout the life test, and are shown in Table 16. Flux and rejection remained essentially unchanged until sometime between points H and I (i.e., about 500 hrs of exposure to various plating bath solutions), when a decrease in both occurred.

During the zinc cyanide life test, membrane flux and total solids rejection were measured daily. These are shown in Figures 49 and 50. The gaps between groups of points indicate interruptions in the life tests for various reasons. Figure 49 shows that flux remained relatively unchanged over the entire life test period. However, the total solids rejection data (Figure 50) showed a significant decline starting at about 500 hrs of exposure.

These life test data with the cyanide bath are considered to be promising, and suggest that if operation is at controlled pH, membrane life would be satisfactory.

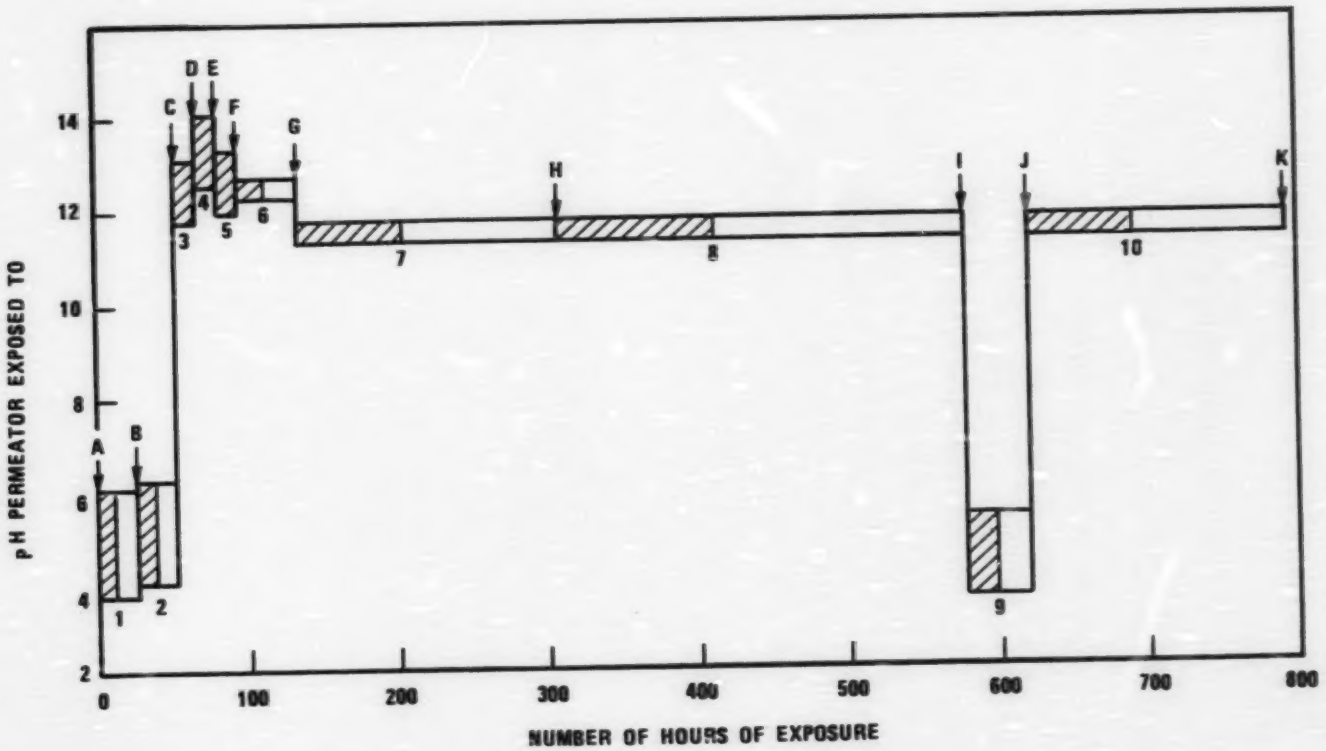

Figure 48. Life Data of B-9 Permeator #3

Table 16. Guide to Figure 48

= System pressurized and in operation

= System exposed to solution at ambient conditions

1	=	Ni $(OSO_2NH_2)_2$ solution
2	=	$ZnCl_2$ solution
3,6	=	$Cd(CN)_2$ solution
4,7,8,10	=	$Zn(CN)_2$ solution
5	=	CuCN solution
9	=	Ni $(BF_4)_2$ solution

	0.5% NaCl Flux, gpm	0.5% NaCl Rejection
A	= 2.50	96%
B	= 2.10	97%
C	= 1.80	98%
D	= 2.60	98%
E	= 2.40	98%
F	= 2.35	98%
G	= 2.20	97%
H	= 2.15	97%
I	= 1.45	90%
J	= 1.20	90%
K	= 1.60	88%

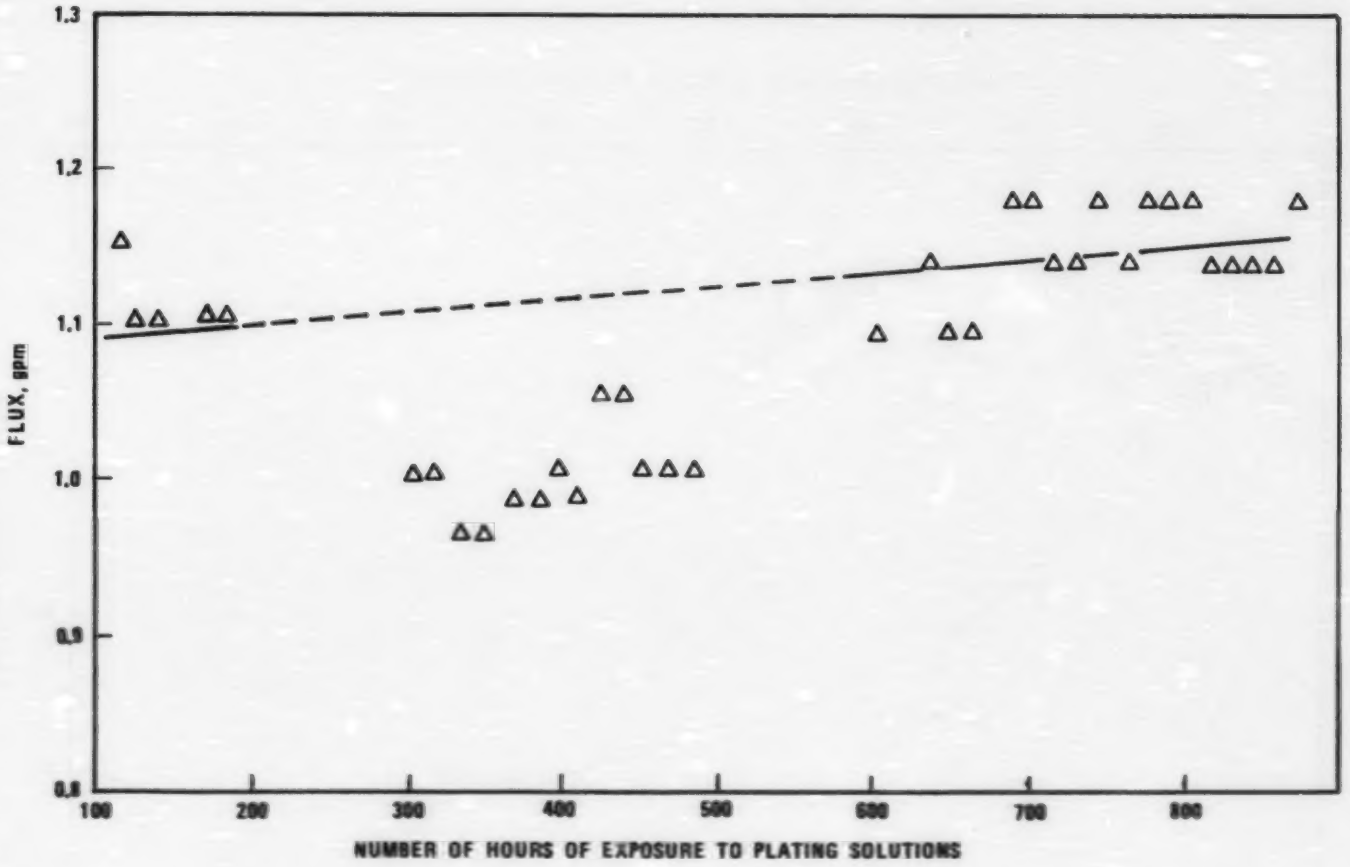

Figure 49. Flux Data in $Zn(CN)_2$ Life Test

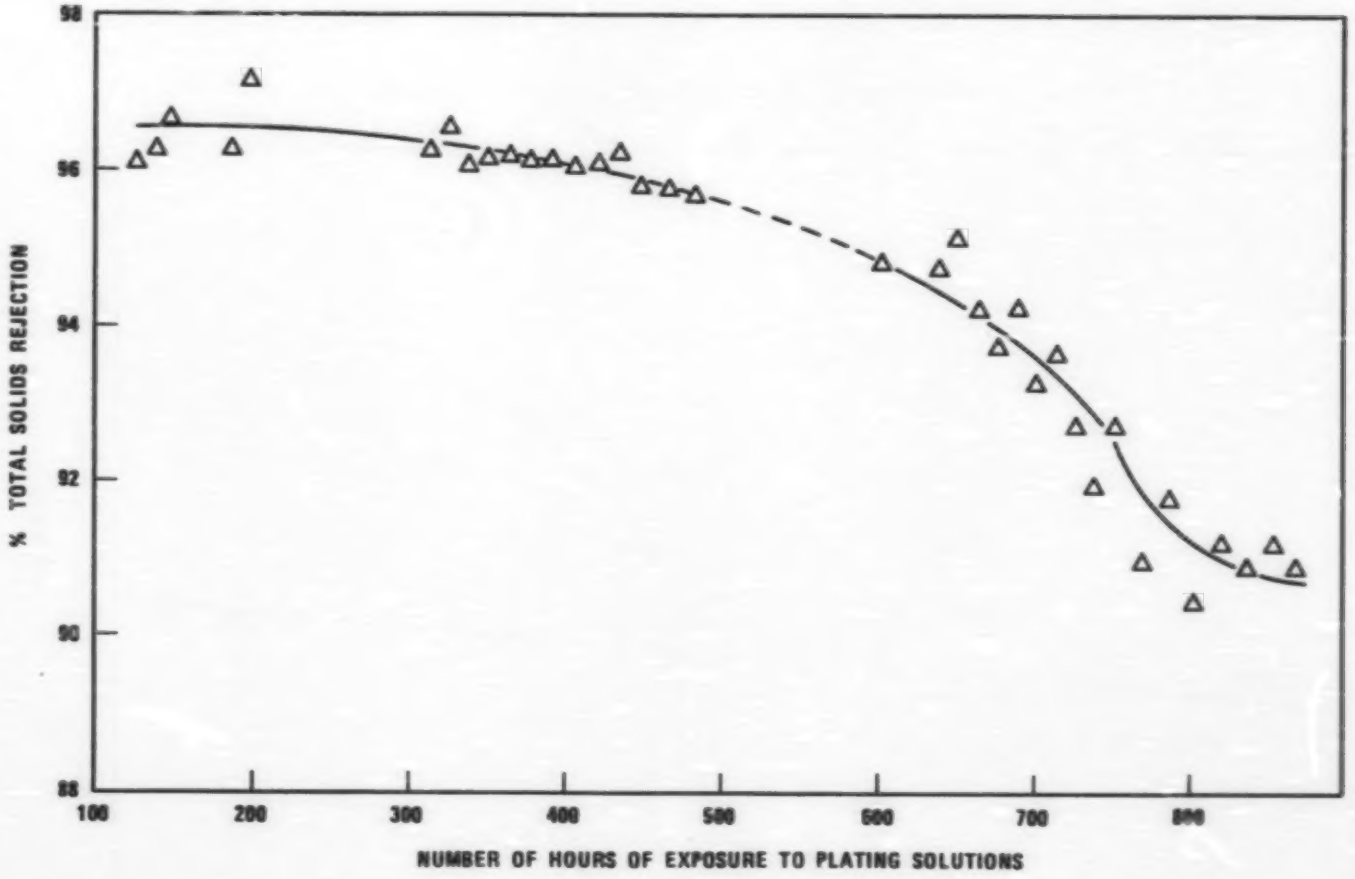

Figure 50. Total Solids Rejection in $Zn(CN)_2$ Life Test

SECTION VI

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16. ABSTRACT
Reverse osmosis treatment of plating bath rinsewaters has been examined. Emphasis has been placed on closed-loop operation with recycle of purified water for rinsing, and return of plating chemical concentrate to the bath. Three commercially available membrane configurations have been evaluated experimentally; tubular (cellulose acetate membrane), spiral-wound (cellulose acetate membrane), and hollow-fiber (polyamide membrane). Tests were conducted with nine different rinsewaters prepared by dilution of actual plating baths. Advantages and limitations of the reverse osmosis process and specific membranes and configurations are discussed. Promising, as well as unattractive applications are indicated.

Systems tested include nickel sulfamate, Watts-type nickel, Copper pyrophosphate, Zinc chloride, copper cyanide, zinc cyanide, cadmium cyanide, nickel fluoborate and chromic acid.

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